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Brueckner doubles coupled cluster method with the polarizable continuum model of solvation

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We present the theory and implementation for computing the (free) energy and its analytical gradients with the Brueckner doubles (BD) coupled cluster method in solution, in combination with the polarizable continuum model of solvation (PCM). The complete model, called PTED, and an efficient approximation, called PTE, are introduced and tested with numerical examples. Implementation details are also discussed. A comparison with the coupled-cluster singles and doubles CCSD-PCM-PTED and CCSD-PCM-PTE schemes, which use Hartree-Fock (HF) orbitals, is presented. The results show that the two PTED approaches are mostly equivalent, while BD-PCM-PTE is shown to be superior to the corresponding CCSD scheme when the HF reference wave function is unstable. The BD-PCM-PTE scheme, whose computational cost is equivalent to *gas phase* BD, is therefore a promising approach to study molecular systems with complicated electronic structure in solution.
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I. INTRODUCTION

A reliable account of the solvent effect in electronic structure calculations is essential not only for energetics (from solvation energies to reaction barriers), but also for the description of molecular structures and properties, from ground and excited state spectroscopies to dynamical processes. At the same time, an accurate representation of the electronic structure of the solute (or supra-molecular aggregate) requires quantum mechanical (QM) methods of possibly high computational cost. The goal of combining the requirements above can be achieved by focusing on what part of the interaction with the solvent has the largest impact on the solute. This, obviously, depends on the type of property of interest: for charge transfer between solute and solvent or other dynamical processes, the electronic structure calculation should be extended at least to some solvent molecules. For other properties, however, the electronic structure of the solvent may not be necessary and a classical description of it as point charges (polarizable or not) may suffice. Even further, the solvent may be described as a bulk material with no atomistic structure when the interaction is mainly long range.

Various models have been presented over the years that describe the solvent at the various levels of approximation mentioned above, coupled with various (quantum or classical) methods to describe the solute. For the latter, coupled cluster (CC) (Refs. 1 and 2) theory has emerged as the preferred choice when an accurate description of the electronic wave function is sought. The CC wave function is obtained by applying an exponential excitation operator on a reference wave function. The excitation manifold is often truncated for practical purposes at a certain level of excitation, and the most widely used truncation includes single and double excitations (CCSD).³ The exponential expansion ensures size-extensivity

at any level of truncation, and includes higher order excited determinants than the corresponding configuration interaction wave function. These features have contributed to the success of CC theory. On the other hand, the computational effort of this approach increases very rapidly with the size of the system (CCSD already scales as $\mathcal{O}(N^6)$, where N is the number of basis functions), limiting the range of systems that can be treated at this level of theory. This is evidently even more problematic when a system is in solution. As mentioned above, a number of approaches have been proposed to combine a CC wave function for the solute with an approximate description of the solvent. Of particular interest is the work of Kongsted *et al.*,⁴⁻⁸ where the solvent is described through a polarizable force field (thus keeping an atomistic description of the solvent); of Slipchenko *et al.*,^{9,10} who used effective fragment potentials; of Christiansen and Mikkelsen,^{11,12} who first introduced the coupling with a polarizable continuum description of the solvent. Recently, Cammi¹³ revisited the latter approach within the framework of the polarizable continuum model (PCM),^{14,15} and extended such approach to the symmetry adapted cluster-configuration interaction approach with Nakatsuji and co-workers.^{16,17} We have also investigated the possibility of combining CC wave function and PCM for ground and excited states.^{18,19}

Discrete and continuum models have their advantages and disadvantages. The former maintain a more realistic description of the solvent, thus allowing for specific solute-solvent interactions (i.e., hydrogen bond), but imply many possible configurations of the solvent molecules, which may require many QM calculations for the solute. Continuum models such as PCM do not require conformational sampling since it is implicit in the solvent macroscopic dielectric constant, and automatically provide mutual solute-solvent polarization. Therefore, they are computationally very efficient, but cannot account for specific solute-solvent interactions. Most likely, the best approach involves the simultaneous use of both

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models. Before that, however, further investigation on how they work independently is still necessary.

Our long experience with continuum models, PCMs in particular, led us to investigate how PCM can be efficiently combined with CC wave functions. We originally followed Cammi's approach for CCSD. Contrary to Christiansen and Mikkelsen,^{11,12} whose model used a *gas phase* reference function (unpolarized orbitals), Cammi proposed to separate the PCM interaction (the solvent *reaction field*) with the reference function (Hartree-Fock, HF) from that with the post-HF expansion. This model, called for historical reasons PTED (Ref. 13) (because it was first proposed in the context of perturbation theory and uses the density to correct the energy), uses polarized orbitals. The post-HF reaction field does not influence the orbitals, similar to *gas phase* CCSD. The CCSD-PCM-PTED model is computationally more expensive than *gas phase* CCSD, since it requires the knowledge of the one-particle reduced density. However, the PTED model can be approximated by neglecting the post-HF reaction field: PTE model. This leads to CCSD equations that are formally the same as those for the *gas phase*, although, the reference energy contains the PCM contribution and the orbitals are polarized. Our implementation and testing of the PTED and PTE models for CCSD (energy and its first derivatives)¹⁹ clearly showed that PTE is a very effective approximation of PTED when HF is a reliable reference. We investigated several systems, including zwitterions, and for all of them the PTE results were very close to those of PTED, at a computational cost comparable to a *gas phase* CCSD calculation.

However, the obvious question arises: What happens when HF is not a reliable reference? CCSD has shown large sensitivity to the choice of the reference function, which may be problematic when systems such as metal complexes are studied and multiple HF solutions are available. Before resorting to multi-reference approaches (for which there are multiple options in CC theory, without a preferred choice yet^{1,2}), there is a variant of CCSD that has shown larger stability with respect to the choice of the reference function: Brueckner doubles (BD).^{20,21} 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). Although there is not a formal proof for such behavior, in practice, BD provides a unique (and thus more reliable) electronic wave function in many cases where CCSD provides multiple solutions (in some cases even when starting from the same reference²²).

The goal of this paper is to introduce the theory for the combination of the BD wave function and PCM. We define the free energy functional for the PTED approach and the PTE approximation, and its analytic gradients. The working equations are presented and some details of their implementation are discussed in Sec. II. The BD-PCM equations are slightly more complicated than the corresponding CCSD ones, due to the inclusion of the orbital rotation. In Sec. III, we present a numerical evidence of the advantage of using BD in difficult cases. We also show that BD works as well as CCSD when

HF is a good reference, by considering some of the systems from our previous study.¹⁹ More importantly, these examples show how PTE is an even better approximation of PTED for BD than for CCSD. BD-PCM-PTE thus represents a promising approach to study coordination chemistry in solution, and other systems where CCSD may suffer from ambiguity in the choice of the most appropriate reference function. Concluding remarks and perspectives on future developments are discussed in Sec. IV.

II. THEORY

The definition of the BD wave function in the presence of the solvent reaction field (modeled by a polarizable continuum dielectric) strictly follows the development presented by Cammi¹³ for a general coupled cluster wave function. Therefore, we adopt the conventions defined in Ref. 13 for the PCM terms, and refer the reader to Cammi's work for more details. We only report the fundamental quantities from Ref. 13 that are necessary for the development of the present theory, and outline the differences with respect to the BD wave function. The details on how to compute the solvent reaction field can also be found in Refs. 15 and 23, as the theory presented in the following can be applied to different versions of PCM. Our implementation includes the integral equation formalism and conductor-like flavors of PCM (IEF-PCM (Refs. 24 and 25) and CPCM,^{26,27} respectively), and makes use of the smooth cavity definition proposed by some of us,²³ and based on the work of York and Karplus.²⁸ Additionally, since, in practice, the presence of the reaction field only adds a few terms to the *gas phase* BD equations, we do not consider it necessary to repeat the latter here. Consequently, we will only report the explicit PCM terms to be added to the *gas phase* BD equations as reported by Kobayashi *et al.* in Ref. 21.

A. PTED free energy functional

The fundamental quantity is the BD-PCM-PTED free energy functional:²⁹

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

where H_0 is the solute Hamiltonian, Φ_{BD}^0 is the BD reference function, $T = T_2$ is the excitation operator (corresponding to double excitations-only for BD), Λ is the Z vector from gradient theory.²¹ $\bar{\mathbf{Q}}(\Lambda, T)$ and $\bar{\mathbf{V}}(\Lambda, T)$ are the PCM reaction field and the solute electrostatic potential on the cavity surface, respectively.¹³ Since both depend on the total BD 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.²¹ 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 remind the reader that the operators are vectors of dimension equal to the number of surface elements.

Before reporting the working equations to compute G_{BD} , let us introduce some useful expressions. In the following, we

will use Einstein's convention for the summation over common indexes. The Fock matrix in the presence of the PCM operator is

$$f_{pq}^{\text{PCM}} = f_{pq} + \mathbf{v}_{pq} \cdot \bar{\mathbf{Q}}^0, \quad (2)$$

where f_{pq} is the solute Fock matrix (but with polarized orbitals), \mathbf{v}_{pq} is the electronic potential on the cavity surface, and $\bar{\mathbf{Q}}^0$ is the reaction field from the reference function and the nuclei. The indexes $pqr \dots$ refer to generic molecular orbitals (MOs), while the letters $ijk \dots$ refer to occupied MOs and $abc \dots$ to virtual MOs. The reference free energy is

$$\begin{aligned} G_{\text{BD}}^0 &= h_{ii} + \frac{1}{2} \langle ij || ij \rangle + V_{nn} + \frac{1}{2} \mathbf{v}_{ii} \cdot \bar{\mathbf{Q}}^0 + \frac{1}{2} \mathbf{V}_n \cdot \bar{\mathbf{Q}}^0 \\ &= E_{\text{BD}}^0 + \frac{1}{2} \mathbf{v}_{ii} \cdot \bar{\mathbf{Q}}^0 + \frac{1}{2} \mathbf{V}_n \cdot \bar{\mathbf{Q}}^0, \end{aligned} \quad (3)$$

where h_{ii} are the one-electron integrals, $\langle ij || ij \rangle$ are the antisymmetrized two-electron integrals, V_{nn} is the nuclear repulsion energy, and $\frac{1}{2} \mathbf{V}_n \cdot \bar{\mathbf{Q}}^0$ is the energy contribution from the interaction of the potential generated by the solute nuclei (\mathbf{V}_n) with the solvent reaction field. Introducing now the normal-product form of an operator,²

$$X_N = X - \langle \Phi_{\text{BD}}^0 | X | \Phi_{\text{BD}}^0 \rangle = X - \bar{X}^0, \quad (4)$$

we have, for the potential,

$$\begin{aligned} \bar{\mathbf{V}}(\Lambda, T) &= \langle \Phi_{\text{BD}}^0 | (1 + \Lambda) e^{-T} \mathbf{V} e^T | \Phi_{\text{BD}}^0 \rangle \\ &= \bar{\mathbf{V}}_N + \bar{\mathbf{V}}^0 \\ &= \gamma_{pq}^\Delta \mathbf{v}_{pq} + \bar{\mathbf{V}}^0, \end{aligned} \quad (5)$$

where $\bar{\mathbf{V}}^0$ includes the contribution from the solute nuclei. γ^Δ is the reduced one-particle density, whose components are (in symmetrized form)

$$\begin{aligned} \gamma_{ij}^\Delta &= -\frac{1}{2} \lambda_{ik}^{ab} t_{jk}^{ab}, \\ \gamma_{ab}^\Delta &= \frac{1}{2} \lambda_{ij}^{ac} t_{ij}^{bc}, \\ \gamma_{ia}^\Delta &= \lambda_i^a + \lambda_j^b t_{ij}^{ab}, \end{aligned} \quad (6)$$

where t and λ are the amplitudes corresponding to the T and Λ operators, respectively. γ^Δ differs from the total BD density in Eqs. (2.32)–(2.34) of Ref. 21 only for the reference density (δ_{ij} term in Eq. (2.32) in Ref. 21). Similarly, for the reaction field:

$$\bar{\mathbf{Q}}(\Lambda, T) = \bar{\mathbf{Q}}_N + \bar{\mathbf{Q}}^0 = \gamma_{pq}^\Delta \mathbf{q}_{pq} + \bar{\mathbf{Q}}^0. \quad (7)$$

Finally, we define

$$\Delta E_{\text{BD}} = \langle \Phi_{\text{BD}}^0 | e^{-T} H_0 e^T | \Phi_{\text{BD}}^0 \rangle = \frac{1}{4} \langle ij || ab \rangle t_{ij}^{ab}, \quad (8)$$

which has the same form of the correlation energy for the *gas phase* BD method. Thus, we can write

$$E_{\text{BD}} = \langle \Phi_{\text{BD}}^0 | e^{-T} H_0 e^T | \Phi_{\text{BD}}^0 \rangle = E_{\text{BD}}^0 + \Delta E_{\text{BD}}, \quad (9)$$

which, in turn, has the same form of the *gas phase* BD energy in Eq. (2.1) in Ref. 21. Note, however, that since the reaction

field depends on the total density,¹¹

$$\langle \Phi_{\text{BD}}^0 | (1 + \Lambda) e^{-T} H_0 e^T | \Phi_{\text{BD}}^0 \rangle \neq \langle \Phi_{\text{BD}}^0 | e^{-T} H_0 e^T | \Phi_{\text{BD}}^0 \rangle, \quad (10)$$

contrary to the *gas phase* case.

In the following, we will use the terminology: *polarized reference* BD expressions, to refer to those expressions that are formally identical to *gas phase* BD, but where the Fock operator includes the PCM operator (f^{PCM} , Eq. (2)) and the orbitals are polarized by the solvent. In order to compute G_{BD} , we need to find the T and Λ amplitudes, and the BD reference function Φ_{BD}^0 . This can be achieved by imposing that G_{BD} is stationary with respect to variations of t , λ , and the MOs. The condition on the MOs ensures that the single excitation amplitudes t_i^a are zero under the perturbation (the reaction field), which is the characteristic of the Brueckner coupled cluster wave function. The partial derivatives of G_{BD} with respect to the singles and doubles λ amplitudes provide the equations for Φ_{BD}^0 and t_{ij}^{ab} :

$$\frac{\partial G_{\text{BD}}}{\partial \lambda_i^a} = b_i^a + \mathbf{v}_{ia} \cdot \bar{\mathbf{Q}}_N + t_{ij}^{ab} \mathbf{v}_{jb} \cdot \bar{\mathbf{Q}}_N = 0, \quad (11)$$

$$\frac{\partial G_{\text{BD}}}{\partial \lambda_{ij}^{ab}} = b_{ij}^{ab} + (t_{ij}^{cb} \mathbf{v}_{ac} \cdot \bar{\mathbf{Q}}_N + t_{ij}^{ac} \mathbf{v}_{cb} \cdot \bar{\mathbf{Q}}_N)$$

$$- (t_{kj}^{ab} \mathbf{v}_{ik} \cdot \bar{\mathbf{Q}}_N + t_{ik}^{ab} \mathbf{v}_{kj} \cdot \bar{\mathbf{Q}}_N) = 0, \quad (12)$$

where b_i^a and b_{ij}^{ab} are the *polarized reference* BD single and double amplitude expressions (left hand side of Eqs. (2.2) and (2.3) in Ref. 21). Equation (11) is used to compute Φ_{BD}^0 by rotating the orbitals until the equation is satisfied. This is accomplished by taking the derivative of Eq. (11) with respect to the orbital rotation and solving the corresponding coupled perturbed BD equations, as reported by Raghavachari *et al.* in Ref. 30 (Eqs. (29) and (30)). The presence of the PCM operators only adds few more terms to the *polarized reference* equations:

$$\begin{aligned} &b_i^a + \mathbf{v}_{ia} \cdot \bar{\mathbf{Q}}_N + t_{ij}^{ab} \mathbf{v}_{jb} \cdot \bar{\mathbf{Q}}_N \\ &+ U_{ck} \left[\left(\frac{\partial b_i^a}{\partial U_{ck}} \right) - 2(\mathbf{v}_{ia} + t_{ij}^{ab} \mathbf{v}_{jb}) \cdot \mathbf{q}_{kc} \right. \\ &+ (\delta_{ac} \mathbf{v}_{ik} - \delta_{ik} \mathbf{v}_{ac} + t_{ij}^{ac} \mathbf{v}_{jk} - t_{ik}^{ab} \mathbf{v}_{bc}) \cdot \bar{\mathbf{Q}}_N \\ &\left. - 2(\mathbf{v}_{ia} + t_{ij}^{ab} \mathbf{v}_{jb}) \cdot (\mathbf{q}_{pc} \gamma_{pk}^\Delta - \mathbf{q}_{pk} \gamma_{pc}^\Delta) \right] = 0. \end{aligned} \quad (13)$$

Equation (13) is the BD-PCM-PTED equivalent of Eq. (29) of Ref. 30. $U_{ck} \left(\frac{\partial b_i^a}{\partial U_{ck}} \right)$ contains the *polarized reference* terms from Eq. (30) of Ref. 30. Equation (12) is solved to compute the t_{ij}^{ab} amplitudes. As for the *gas phase* case, Eqs. (11)–(13) are solved iteratively until convergence.

The partial derivatives of the free energy functional with respect to the orbital rotation U_{ai} and the t_{ij}^{ab} amplitudes provide the equations for the λ_i^a and λ_{ij}^{ab} amplitudes:

$$\begin{aligned} \frac{\partial G_{\text{BD}}}{\partial U_{ai}} &= \lambda_k^c \left(\frac{\partial b_k^c}{\partial U_{ai}} \right) + 2 \tilde{\lambda}_k^c \mathbf{v}_{kc} \cdot \mathbf{q}_{ia} \\ &+ \frac{1}{2} (\tilde{\lambda}_i^c \mathbf{v}_{ca} - \tilde{\lambda}_k^a \mathbf{v}_{ik}) \cdot \bar{\mathbf{Q}}_N \end{aligned}$$

$$\begin{aligned}
& + \tilde{\lambda}_k^c \mathbf{v}_{kc} \cdot (\mathbf{q}_{pa} \gamma_{pi}^\Delta - \mathbf{q}_{pi} \gamma_{pa}^\Delta) + \frac{1}{4} \lambda_{jk}^{bc} \left(\frac{\partial b_{jk}^{bc}}{\partial U_{ai}} \right) \\
& + \frac{1}{2} \mathcal{S}(\lambda, t) [\lambda_{kj}^{cb} (t_{kj}^{db} \mathbf{v}_{dc} - t_{lj}^{cb} \mathbf{v}_{kl}) \cdot \mathbf{q}_{ia}] \\
& - \frac{1}{4} \mathcal{S}(\lambda, t) [\lambda_{kj}^{cb} (t_{kj}^{ab} \mathbf{v}_{ic} + t_{ij}^{cb} \mathbf{v}_{ka}) \cdot \bar{\mathbf{Q}}_N] \\
& + \frac{1}{2} \lambda_{kj}^{cb} (t_{kj}^{cd} \mathbf{v}_{db} - t_{lj}^{cb} \mathbf{v}_{kl}) \cdot (\mathbf{q}_{pa} \gamma_{pi}^\Delta - \mathbf{q}_{pi} \gamma_{pa}^\Delta) \\
& + \left(\frac{\partial E_{BD}}{\partial U_{ai}} \right) - \mathbf{v}_{ia} \cdot \bar{\mathbf{Q}}_N - t_{ij}^{ab} \mathbf{v}_{jb} \cdot \bar{\mathbf{Q}}_N = 0,
\end{aligned} \tag{14}$$

$$\begin{aligned}
\frac{\partial G_{BD}}{\partial t_{ij}^{ab}} &= \lambda_k^c \left(\frac{\partial b_k^c}{\partial t_{ij}^{ab}} \right) + (\lambda_i^a \mathbf{v}_{jb} - \lambda_i^b \mathbf{v}_{ja} - \lambda_j^a \mathbf{v}_{ib} + \lambda_j^b \mathbf{v}_{ia}) \cdot \bar{\mathbf{Q}}_N \\
& + \frac{1}{4} \lambda_{kl}^{cd} \left(\frac{\partial b_{kl}^{cd}}{\partial t_{ij}^{ab}} \right) + (\lambda_{ij}^{ad} \mathbf{v}_{db} + \lambda_{ij}^{db} \mathbf{v}_{ad} - \lambda_{kj}^{ab} \mathbf{v}_{ik} \\
& - \lambda_{ik}^{ab} \mathbf{v}_{kj}) \cdot \bar{\mathbf{Q}}_N + \left(\frac{\partial E_{BD}}{\partial t_{ij}^{ab}} \right) = 0,
\end{aligned} \tag{15}$$

where $\lambda_k^c \left(\frac{\partial b_k^c}{\partial U_{ai}} \right)$, $\frac{1}{4} \lambda_{jk}^{bc} \left(\frac{\partial b_{jk}^{bc}}{\partial U_{ai}} \right)$, and $\left(\frac{\partial E_{BD}}{\partial U_{ai}} \right)$ are the terms of the *polarized reference* BD equations for the Λ_1 amplitudes, and $\lambda_k^c \left(\frac{\partial b_k^c}{\partial t_{ij}^{ab}} \right)$, $\frac{1}{4} \lambda_{kl}^{cd} \left(\frac{\partial b_{kl}^{cd}}{\partial t_{ij}^{ab}} \right)$, and $\left(\frac{\partial E_{BD}}{\partial t_{ij}^{ab}} \right)$ are the terms of the *polarized reference* BD equations for the Λ_2 amplitudes (Eqs. (2.13)–(2.26) in Ref. 21). In Eq. (14) we used

$$\tilde{\lambda}_i^a = \gamma_{ia}^\Delta = \lambda_i^a + \lambda_j^b t_{ij}^{ab}, \tag{16}$$

and the permutation symmetrization operator

$$\mathcal{S}(x, y) f(x, y) = f(x, y) + f(y, x). \tag{17}$$

By using Eqs. (3) and (8) with the conditions in Eqs. (11) and (12), after simple algebra, Eq. (1) can be recast in a simpler form (which does not require the calculation of the two-particle density):

$$G_{BD} = G_{BD}^0 + \Delta E_{BD} - \frac{1}{2} \bar{\mathbf{V}}_N \cdot \bar{\mathbf{Q}}_N. \tag{18}$$

A comment is also in order concerning the derivative of the PCM energy contribution with respect to a generic parameter ξ . In the above equations, we implicitly assumed

$$\frac{\partial}{\partial \xi} \left(\frac{1}{2} \bar{\mathbf{V}}(\xi) \cdot \bar{\mathbf{Q}}(\xi) \right) = \bar{\mathbf{V}}^\xi(\xi) \cdot \bar{\mathbf{Q}}(\xi). \tag{19}$$

This is correct in operator form (i.e., before discretization of the cavity surface) since the reaction field is related to the solute potential by³¹

$$U^{\text{PCM}} \bar{\mathbf{Q}}(\xi) = \bar{\mathbf{V}}(\xi) \tag{20}$$

and U^{PCM} is self-adjoint.^{15,32} This is not the case, however, in the discretized form of the IEF equations as usually reported in the literature (i.e., the matrix \mathbf{U}^{IEF} is not symmetric¹⁵). We avoided this problem by employing the symmetrized version of the IEF equations as suggested by Lipparini *et al.*,³² so that

Eq. (19) also applies in the discretized form. Additionally, this problem does not arise for the conductor-like version of PCM (CPCM) since the \mathbf{U}^{CPCM} matrix is intrinsically symmetric.

B. PTE approximation

As for CCSD, it is possible to introduce a PTE approximation by neglecting the correlation reaction field $\bar{\mathbf{Q}}_N$. This corresponds to considering the solvent contribution only in the reference function through the PCM operator in the Fock operator (Eq. (2)). This approximation has several computational advantages, as the part of the reaction field that depends on the reduced density γ^Δ is neglected. Since γ^Δ is no longer needed, the equality in Eq. (10) is restored and the Λ vector is not necessary to compute G_{BD} . Indeed, Eqs. (1) and (18) reduce to the following:

$$G_{BD}^{\text{PTE}} = G_{BD}^0 + \Delta E_{BD}. \tag{21}$$

Also, Eqs. (11) and (12) reduce to the *polarized reference* case:

$$\frac{\partial G_{BD}^{\text{PTE}}}{\partial \lambda_i^a} = b_i^a = 0, \tag{22}$$

$$\frac{\partial G_{BD}^{\text{PTE}}}{\partial \lambda_{ij}^{ab}} = b_{ij}^{ab} = 0. \tag{23}$$

However, the presence of the PCM operator in the Fock operator implies that, when the derivative of Eq. (22) with respect to the orbital rotation to compute Φ_{BD}^0 is taken, the proper derivative of the PCM operator must be included. Thus, Eq. (13) becomes

$$b_i^a + U_{ck} \left[\left(\frac{\partial b_i^a}{\partial U_{ck}} \right) - 2(\mathbf{v}_{ia} + t_{ij}^{ab} \mathbf{v}_{jb}) \cdot \mathbf{q}_{kc} \right] = 0. \tag{24}$$

The PTE approximation *de facto* reduces the computational cost of each step in the iterative solution of Eqs. (11) and (12) to the *gas phase* actual cost, as the extra computational effort introduced by the PCM terms in Eqs. (2) and (24) is negligible, as shown in Sec. II D. Nonetheless, the PTE model maintains the attractive feature of the BD-PCM approach, that is the more direct coupling of the solvent effect on the MOs with the CC expansion.

C. Free energy analytical gradients

The analytical gradient expression of the PTED free energy functional in Eq. (1) with respect to an external perturbation directly follows Cammi's derivation for the CCSD free energy functional.¹³ The extra terms due to the PCM operators are the same for CCSD and BD; therefore, we do not find necessary to repeat the same equations again. We only point out that, as for the *gas phase* case, in BD the orbital relaxation is coupled with the T amplitudes relaxation through Eqs. (14) and (15). Thus, γ^Δ (Eq. (6)) already includes the orbital response.

Although, some comments are necessary for the PTE approximation. As in the case of CCSD, BD-PCM-PTE does

not require the Λ vector for the calculation of the free energy, but this vector is necessary for the evaluation of the free energy analytical gradients. Contrary to CCSD, however, the λ_i^a equation for BD-PCM-PTE is slightly different than that for the *gas phase*:

$$\begin{aligned} \frac{\partial G_{\text{BD}}^{\text{PTE}}}{\partial U_{ai}} &= \lambda_k^c \left(\frac{\partial b_k^c}{\partial U_{ai}} \right) + 2\tilde{\lambda}_k^c \mathbf{v}_{kc} \cdot \mathbf{q}_{ia} + \frac{1}{4} \lambda_{jk}^{bc} \left(\frac{\partial b_{jk}^{bc}}{\partial U_{ai}} \right) \\ &+ \frac{1}{2} \mathcal{S}(\lambda, t) [\lambda_{kj}^{cb} (t_{kj}^{db} \mathbf{v}_{dc} - t_{lj}^{cb} \mathbf{v}_{kl}) \cdot \mathbf{q}_{ia}] \\ &+ \left(\frac{\partial E_{\text{BD}}}{\partial U_{ai}} \right) = 0. \end{aligned} \quad (25)$$

The PCM terms in Eq. (25) come from the derivative of the PCM term in the Fock operator, Eq. (2).

D. Implementation of the PCM terms

Although the PTED model couples Eqs. (11)–(15), and thus the evaluation of the free energy is more expensive than the *gas phase* energy, the added computational cost of the individual PCM terms is small. In fact, the calculation of the reaction field ($\bar{\mathbf{Q}}_N$ or $\bar{\mathbf{Q}}^0$) has been shown to be fast compared to the Fock matrix formation.²³ Also, the terms in these equations reuse intermediates that are already evaluated for the *polarized reference* part of the equations. For example, for the term in Eq. (14),

$$-\frac{1}{4} \mathcal{S}(\lambda, t) [\lambda_{kj}^{cb} (t_{kj}^{ab} \mathbf{v}_{ic} + t_{ij}^{cb} \mathbf{v}_{ka}) \cdot \bar{\mathbf{Q}}_N], \quad (26)$$

the expensive intermediates $\lambda_{kj}^{cb} t_{kj}^{ab}$ and $\lambda_{kj}^{cb} t_{ij}^{cb}$ (which scale as $o^2 v^3$ and $o^3 v^2$, respectively, where o is the number of occupied MOs and v is the number of virtual MOs) are also needed for the *polarized reference* equations. Thus, the contraction with the PCM operator is performed when these intermediates become available. While, for other terms like in Eq. (12),

$$t_{ij}^{cb} \mathbf{v}_{ac} \cdot \bar{\mathbf{Q}}_N, \quad (27)$$

the PCM element $\mathbf{v}_{ac} \cdot \bar{\mathbf{Q}}_N$ can be added to an intermediate of the *polarized reference* equation (in particular, to the intermediate in $Q_{ij}^{ab}(I, a \times a)$ in Eq. (2.3). in Ref. 21), so that the contraction with the t_{ij}^{cb} amplitudes ($o^2 v^3$ scaling) is performed only once. The terms where the $t\lambda$ intermediate (already available) is completely contracted with the potential as, for instance, in Eq. (14),

$$+ \frac{1}{2} \lambda_{kj}^{cb} (t_{kj}^{cd} \mathbf{v}_{db} - t_{lj}^{cb} \mathbf{v}_{kl}) \cdot (\mathbf{q}_{pa} \gamma_{pi}^{\Delta} - \mathbf{q}_{pi} \gamma_{pa}^{\Delta}) \quad (28)$$

can be rearranged by considering the intermediate as a pseudo-density ($\lambda_{kj}^{cb} t_{kj}^{cd} = \tilde{\gamma}_{bd}$ and $\lambda_{kj}^{cb} t_{lj}^{cb} = \tilde{\gamma}_{kl}$), and using the symmetry of the PCM operator with respect to the potential (as in Eqs. (19) and (20)) to give

$$+ \frac{1}{2} (\bar{\mathbf{Q}}(\tilde{\gamma}_{db}) - \bar{\mathbf{Q}}(\tilde{\gamma}_{kl})) \cdot (\mathbf{v}_{pa} \gamma_{pi}^{\Delta} - \mathbf{v}_{pi} \gamma_{pa}^{\Delta}), \quad (29)$$

so that the scaling of this term is $O(o^2 v + o v^2)$. Similarly, a term like

$$\frac{1}{2} \mathcal{S}(\lambda, t) [\lambda_{kj}^{cb} (t_{kj}^{db} \mathbf{v}_{dc} - t_{lj}^{cb} \mathbf{v}_{kl}) \cdot \mathbf{q}_{ia}] \quad (30)$$

from Eqs. (14) and (25) can be rearranged as

$$\frac{1}{2} (\bar{\mathbf{Q}}(\tilde{\gamma}_{cd}) - \bar{\mathbf{Q}}(\tilde{\gamma}_{kl})) \cdot \mathbf{v}_{ia}, \quad (31)$$

where

$$\begin{aligned} \mathcal{S}(\lambda, t) [\lambda_{kj}^{cb} t_{kj}^{db}] &= \tilde{\gamma}_{cd}, \\ \mathcal{S}(\lambda, t) [\lambda_{kj}^{cb} t_{lj}^{cb}] &= \tilde{\gamma}_{kl}. \end{aligned} \quad (32)$$

The evaluation of γ^{Δ} (Eq. (6)) requires $\mathcal{O}(N^5)$ work. However, γ^{Δ} can be updated every few iterative cycles during the solution of Eqs. (11)–(15), thus keeping the computational cost of its evaluation in the noise.

Since the leading terms in Eqs. (11)–(15), which scale as $O(o^2 v^4 + o^3 v^3)$ and need to be evaluated at each iterative cycle, are the same as in *gas phase* BD, the evaluation of the extra PCM terms is basically free compared to *gas phase* BD. No appreciable difference can be detected in an iterative step of a *gas phase* or PCM calculation. For the PTE approximation, which simplifies most of the equations as discussed in Sec. II B, the computational cost difference between PCM and *gas phase* BD is virtually eliminated. Additionally, the extra work for the PCM terms in the analytical gradients is negligible compared to the solution of the T and Λ equations and the evaluation of the BD two-particle density matrix. We tested the correctness of the analytical gradients implementation for both PTED and PTE models by comparing the forces on the nuclei with those calculated with numerical gradients.

Finally, our implementation makes use of the Abelian point group symmetry³³ and can handle restricted closed shell and unrestricted wave functions. The methods presented in these sections were implemented in a development version of the GAUSSIAN suite of programs.³⁴

III. RESULTS

In this section we present various tests to demonstrate the efficacy of the methods presented above. We start with some examples from our previous work on the implementation and testing of the CCSD-PCM-PTED and CCSD-PCM-PTE methods.¹⁹ In particular, we investigate the calculation of solvation free energies for five organic molecules in various solvents of increasing polarity, and the stabilization energy of the zwitterionic form of glycine in water. For one of these molecules (pyridine), we also show convergence trends for the BD-PCM-PTED and -PTE schemes. Next, we analyze an extremely simple model: H_3^+ , for which *gas phase* CCSD and BD are equivalent to the full configuration interaction (CI) method. Finally, a more realistic model system is studied: a dihydrogen complex of Fe^+ . These examples are used to compare the performance of BD-PCM with CCSD-PCM for the two PTED and PTE approaches. The PCM cavity was built of interlocking spheres centered on each nucleus with Universal Force Field (UFF) radii.³⁵ No extra spheres were added unless

TABLE I. Solvation free energy (kcal/mol).

	Cyc/ IEF ^a	Dce/ IEF ^a	H ₂ O/ IEF ^a	Cyc/ SMD ^a	Dce/ SMD ^a	H ₂ O/ SMD ^a
Pyridine						
Expt. ^b	-4.30	-5.53	-4.70	-4.30	-5.53	-4.70
PTE	-1.79	-4.10	-4.79	-4.47	-6.76	-4.95
PTED	-1.80	-4.11	-4.80	-4.48	-6.77	-4.96
Aniline						
Expt. ^b	-5.52	-7.39	-5.49	-5.52	-7.39	-5.49
PTE	-1.94	-4.54	-5.35	-5.15	-8.22	-4.73
PTED	-1.94	-4.55	-5.36	-5.16	-8.23	-4.74
Phenol						
Expt. ^b	-5.57	-7.48	-6.62	-5.57	-7.48	-6.62
PTE	-2.17	-4.98	-5.83	-5.38	-8.10	-6.23
PTED	-2.17	-4.99	-5.84	-5.38	-8.10	-6.24
P-bromophenol						
Expt. ^b	-7.14	-9.10	-7.13	-7.14	-9.10	-7.13
PTE	-2.42	-5.44	-6.33	-6.70	-9.49	-7.03
PTED	-2.42	-5.45	-6.34	-6.70	-9.50	-7.04
Chlorobenzene						
Expt. ^b	-5.10		-1.12	-5.10		-1.12
PTE	-0.97	-2.19	-2.55	-5.20	-6.31	-1.10
PTED	-0.98	-2.19	-2.55	-5.21	-6.32	-1.11

^aCyc: cyclohexane; Dce: dichloroethane; IEF: electrostatic-only, UFF radii; SMD: SMD nonelectrostatic and radii.

^bReference 36.

otherwise specified. The continuous surface charge (CSC) scheme described in Ref. 23 was employed.

A. Solvation ΔG and glycine

As in Ref. 19, we compute the solvation free energies (ΔG) (Ref. 37) for five aromatic molecules: pyridine, aniline, phenol, *p*-bromophenol, and chlorobenzene, in three solvents of increasing polarity: cyclohexane (cyc, $\epsilon = 2.02$), dichloroethane (dce, $\epsilon = 10.13$), and water (H_2O , $\epsilon = 78.36$). The calculations are carried out in the same conditions as in Ref. 19: 6-31+G(d,p) basis set, geometry optimized in the corresponding medium, IEF version of PCM. Since IEF-PCM only accounts for electrostatic interactions with the solvent, we also use the Solvation Model Density (SMD) model of Truhlar and co-workers³⁶ to consider nonelectrostatic effects, which are important for low polar solvents. The results for BD-PCM-PTED and BD-PCM-PTE are reported in Table I. The agreement with the experimental data is very good, considering the small basis set used (the effect of the basis set was analyzed in Ref. 19, and is beyond the scope of this work). The importance of nonelectrostatic contributions to the solvation free energy is evident from the results in cyclohexane and dichloroethane, with differences of about 4.5 kcal/mol in some cases. SMD recovers most of these effects, even if it was not parameterized for this level of theory. However, here we are more interested in the comparison between the various methods. BD-PCM-PTED and CCSD-PCM-PTED provide very similar results (compare with Table 1 in Ref. 19), the largest difference being 0.04 kcal/mol for aniline and *p*-bromophenol in water. The equilibrium geometries from the two levels of theory are also basically the same. The agreement of the PTE approximation with the PTED model is

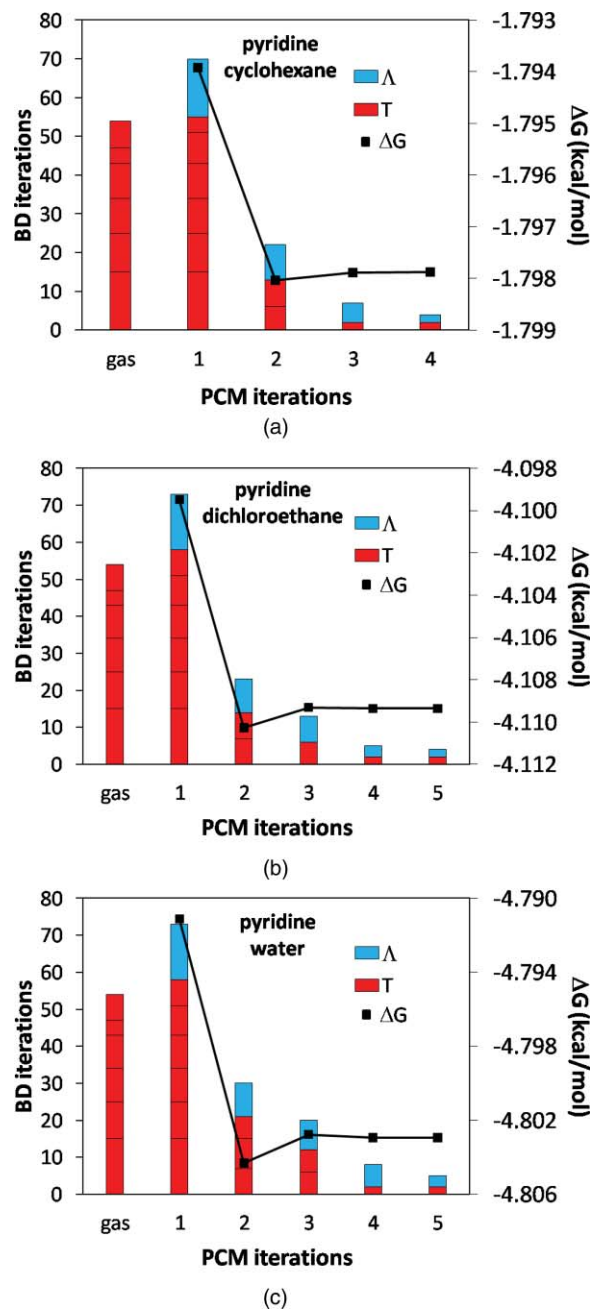


FIG. 1. Convergence of the BD-PCM-PTED scheme for pyridine in different solvents. The first column (“gas”) reports the convergence of the gas phase BD calculation. The red bar in the second column (“1”) reports the convergence of the BD-PCM-PTE approximation, which is the first step of the PTED scheme.

remarkable, always within 0.01 kcal/mol. This is even better than for CCSD, where the difference between PTE and PTED could reach 0.09 kcal/mol.

The convergence of the PTED scheme is shown for pyridine in the three solvents (IEF-PCM) in Fig. 1. The convergence thresholds are 10^{-6} for the wave function and 10^{-8} a.u. for the energy. The red bars report the number of iterations to compute the T amplitudes, and are divided in sections for each BD iteration necessary to compute the reference function Φ_{BD}^0 . The number of T iterations for the *gas phase* calculations is also reported as reference. The red bar of the first iteration of the PTED scheme (column “1” in each plot) is the PTE

TABLE II. Stabilization free energy (kcal/mol) of the zwitterionic form of glycine with respect to the neutral form in water.

Expt. ^a	PTE	PTED
-7.2	-2.07	-2.08

^aReference 38.

approximation. The latter is almost equivalent to a *gas phase* calculation. On the other hand, PTED requires several iterations to converge. However, since PTE is already very close to the PTED solution, the number of steps to compute the T and Λ vectors for each PCM iteration decreases rapidly after the first iteration. Summing all the iterations for T and Λ , PTED roughly requires twice the computational effort compared to the PTE approximation (although, a Λ iteration is more expensive than a T iteration²¹).

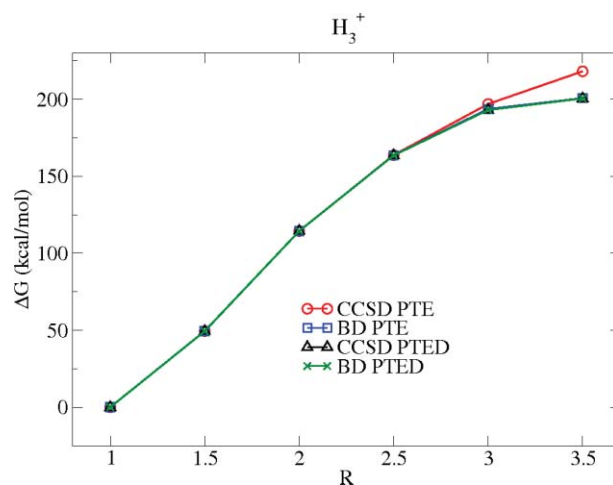
The second example that we take from Ref. 19 is the stabilization of the zwitterionic form of glycine in water with respect to the neutral form. The results for BD are reported in Table II (the 6-31+G(d,p) basis set was used for the calculation). The model here is very crude, since it ignores specific solute-solvent interactions and only one conformer for each glycine form is considered. However, also in this case we are only interested in the relative performance of the methods. A bare PCM approach already provides a qualitatively correct picture, with the zwitterionic form more stable than the neutral form in solution (the zwitterion is not a stable structure in *gas phase*). The difference between BD and CCSD is on the order of 0.2 kcal/mol, much smaller than the error with the experiment. Also, the difference between PTE and PTED is very small, 0.01 kcal/mol, similar to the CCSD case.

These two sets of examples show that BD-PCM is basically equivalent to CCSD-PCM for well behaved cases. PTE is a very good approximation of PTED even in potentially difficult cases such as the zwitterion, and the difference PTE-PTED is even smaller for BD than for CCSD.

B. A very simple system: H_3^+

H_3^+ can be considered the smallest example of 3 center-2 electron bond (3c-2e).³⁹ Obviously, it does not represent a physically meaningful system, especially in water solution. However, it is an interesting model system for this study since both *gas phase* CCSD and BD are equivalent to the exact (within the finite basis set expansion and Born-Oppenheimer approximation) full CI wave function. Therefore, their energy does not depend on the choice of the reference function. This applies also to the PCM-PTED model, but not to the PTE approximation, since the PCM operators in the CC expansion are neglected.

We optimized the geometry of the system in water, maintaining the H centers symmetrically distributed around the center of mass (c.m.) ($r_{c.m.-H}^0 = 0.4966 \text{ \AA}$, $H\widehat{c.m.}H = 120^\circ$). All the calculations were performed with the aug-cc-pVTZ basis set.⁴⁰ The optimizations with all methods provided the same equilibrium geometry. From this conformation, we compute the free energy in solution at various points by increasing the distance from the center of mass ($R \times r_{c.m.-H}^0$, where

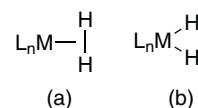
FIG. 2. Free energy change (kcal/mol) in water at various $r_{c.m.-H}$ ($R \times r_{c.m.-H}^0$, where R is a scaling factor).

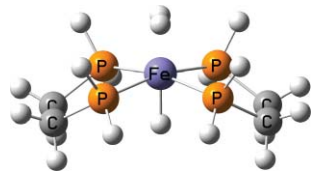
R is a scaling factor). In order to avoid “solvent pockets” at larger distances, an extra sphere is added at all points centered at the center of mass and with a radius equal to the distance to the H nuclei. The free energy profile is reported in Fig. 2 (the reference energy is that at the equilibrium geometry). The four methods agree up to a scaling factor of 2.5. At $R = 3$, CCSD-PCM-PTE differs from the other methods by about 4 kcal/mol, and such difference increases at longer distances. The HF reference has a restricted-unrestricted (RHF-UHF) instability at factors between 2.5–3, since the exact wave function has a growing contribution from the same-spin configuration. This is not a problem for the PTED method, as mentioned above, but it is for PTE. CCSD with the restricted closed-shell reference is not able to correct for this behavior, and the situation worsens at longer distances. On the other hand, the coupling of the reference function with the configuration expansion in BD compensates for the deficiencies of the starting reference function, and the BD-PCM-PTE curve agrees with the PTED curves even starting from the unstable RHF wave function.

C. A more realistic system: Fe- H_2 complex

The H_3^+ example in Sec. III B is a model for σ -bond coordination chemistry, where dihydrogen bonds to a metal center.³⁹ This chemistry is of large interest for hydrogen storage applications, and detailed discussions can be found in excellent review articles.^{39,41-43} Briefly, the H-H bond can split to give a dihydride complex or remain nearly intact, giving a dihydrogen complex, see Fig. 3.

The stability of the η^2 complex depends on the relative strength of σ donation vs. backdonation, i.e., donation of elec-

FIG. 3. Metal-dihydrogen and metal-dihydride complexes. (a) η^2 - H_2 (b) dihydride complex.

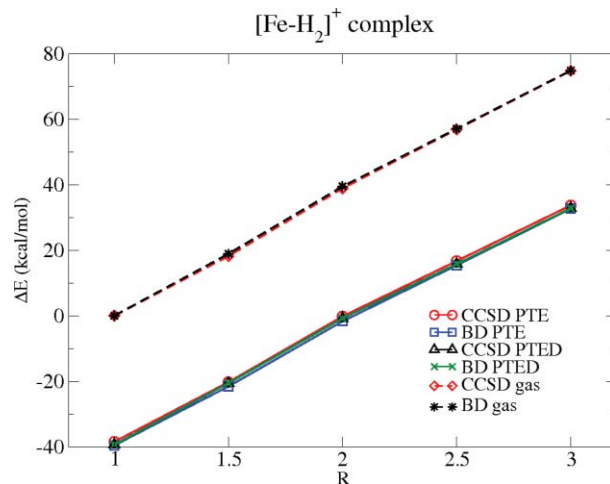
FIG. 4. Structure of the $\text{H}_2[\text{FeH}(\text{PP})_2]^+$ complex.

trons from metal d orbitals to the H_2 σ^* orbital. Too strong backdonation leads to homolytic cleavage of the H–H bond to form the dihydride complex. The balance between these two competing factors depends on the nature of the metal and the ligands, especially to that trans to H_2 . Elongated dihydrogen complexes also exist, where H_2 has large mobility. Most of these reactions happen in solution, and the complexity of the electronic structure of these compounds often requires high level theoretical calculations for the interpretation of experiments. Thus, we choose a model system from this class of complexes to further test the BD-PCM method. We are not (yet) interested in studying real chemical problems, but rather in comparing the BD and CCSD results.

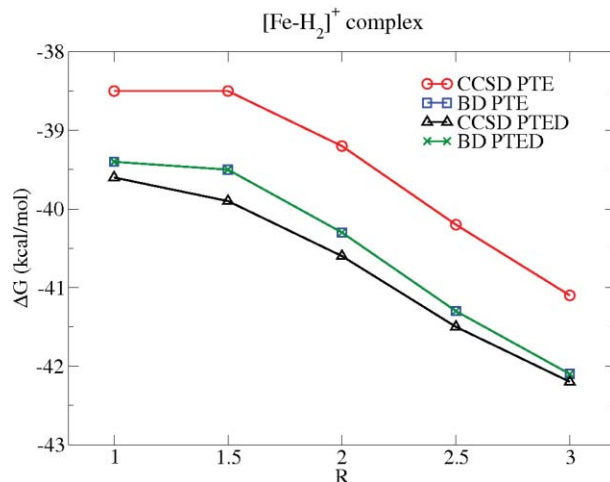
We consider a trans-hydride complex of Fe^+ : $\text{H}_2[\text{FeH}(\text{PP})_2]^+$, as a model for the phenyl diphosphines complex, known to be stable in tetrahydrofuran (THF) solution.^{39,41} The geometry, shown in Fig. 4, was optimized at B3LYP (Refs. 44 and 45) level using the Stuttgart/Dresden pseudopotential⁴⁶ 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 same basis sets are used in the following single point calculations), imposing C_{2v} symmetry. The optimized geometry is available in the supplementary material.⁴⁷ The H–H equilibrium distance is 0.8105 Å, in reasonable agreement with the reported experimental value (0.86–0.97 Å),^{39,41} while the Fe–H₂ distance is 1.6219 Å. Single point energy calculations were then carried out for the isolated molecule and in THF by increasing the H–H bond distance. As for the H_3^+ case, 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 distance). This scan can be considered a very crude model for the H–H bond cleavage.

The change in energy when scaling the H–H distance by a factor R is shown in Fig. 5. The energy increases at longer H–H bond lengths (the reference energies are those at the equilibrium distance in gas phase at the corresponding level of theory), which is consistent with the experimentally known stability of the Fe–H₂ complex. The solvation free energies, calculated as the THF–*gas phase* energy differences for each H–H bond length and level of theory, are reported in Fig. 6. The RHF reference is used as a starting point in all the calculations. The solvent stabilizes more the elongated structures, probably because the electron density is more polarizable. The results show a very good agreement between BD- and CCSD-PCM-PTED at all distances. On the other hand, only BD-PCM-PTE is able to follow the same trend, while CCSD-PCM-PTE is always about 1–1.5 kcal/mol higher in energy.

At $R = 2$ the RHF wave function becomes unstable. The RHF-UHF instability is again due to the constraint of double

FIG. 5. Energy change (kcal/mol) in the $\text{H}_2[\text{FeH}(\text{PP})_2]^+$ complex, in gas and in THF, at various H–H bond distances. R is a scaling factor from the equilibrium bond distance.

occupancy of the orbitals in RHF, as in the H_3^+ case. However, now CCSD and BD are not equivalent to the full CI solution, and the results may vary considerably. BD is not affected by this instability, and the (free) energies are unchanged when starting from the UHF reference both in *gas phase* and in THF, at all of the geometries. This is not the case for CCSD, where both the *gas phase* and solution (free) energies depend on the choice of the reference. The change in energies with the UHF and RHF references, both in *gas phase* and in THF, are reported in the supplementary material.⁴⁷ The solvation free energies computed starting from the RHF and UHF wave functions are shown in Fig. 7. For the PTED approach, the solvation ΔG does not vary considerably (the largest difference, for $R = 3$, is 0.3 kcal/mol), but a CCSD with UHF reference calculation is ~ 3 times more expensive than a CCSD with RHF reference one. The PTE model, on the other hand, provides very different results with the two reference functions, emphasizing the difficulty of CCSD in this case. A comparison between Figs. 6 and 7 shows

FIG. 6. 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.

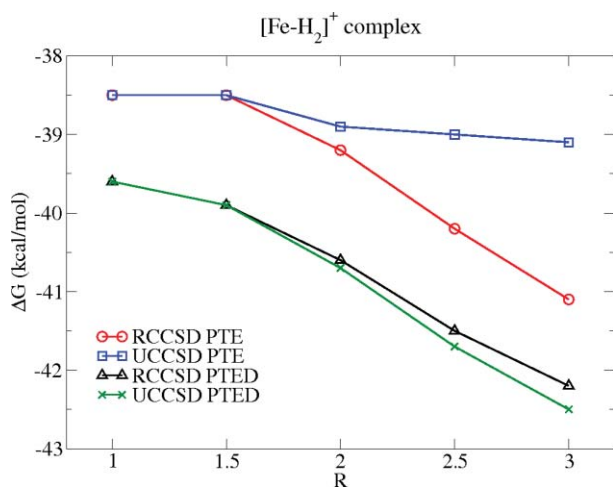


FIG. 7. Solvation free energy (kcal/mol) for the $\text{H}_2[\text{FeH}(\text{PP})_2]^+$ complex at various H–H bond distances for CCSD with the unstable and stable HF references (RHF and UHF, respectively). R is a scaling factor from the equilibrium bond distance.

that reliable solvation free energies can be obtained with the computationally efficient BD-PCM-PTE approach. Note also that we chose a complex with a relatively simple electronic structure, in the sense that it is a stable closed shell system at the equilibrium geometry. The situation may be far more complicated for metals with unpaired d electrons, so that multiple HF solutions may be found. In those cases, the BD insensitivity to the choice of the reference may become even more important.

IV. CONCLUSIONS

In this work, we present the theory, the implementation, and numerical tests for the BD-PCM method. The free energy functional and its analytical gradients are introduced, and details of the implementation are discussed. BD-PCM allows for the study of molecular systems in solution by treating the solute wave function at a high level of theory while taking into account the bulk effect of the solvent in a computationally efficient manner. The complete scheme, PTED, and its approximation, PTE, which includes the PCM contribution only in the reference function, are tested and compared to their corresponding CCSD approaches.^{13,19}

The results reported in this paper show that BD-PCM is equivalent to CCSD-PCM when the HF wave function is a good reference. However, BD-PCM is superior when HF has instabilities that affect the CCSD results, similar to *gas phase*. The more direct coupling of the reference function with the cluster expansion in BD also makes the PTE results almost indistinguishable from those of the PTED scheme. PTE is practically equivalent to the *gas phase* method from the computational effort point of view. Therefore, this approach introduces the often essential solvent effect at almost no cost.

Some caution must be exercised when using electrostatic continuum solvation models if specific interactions between solute and solvent occur, as for the glycine case in Sec. III A, where hydrogen bond interactions are obviously missing. Another case is when low polar solvents are considered, as for

the solvation free energy of aromatic compounds in Sec. III A, where nonelectrostatic contributions are necessary to reproduce the experimental trends. Keeping such considerations in mind, BD-PCM, especially with the PTE scheme, represents a promising method to study systems in solution with a complicated electronic structure, such as coordination chemistry of metals and other open shell species.

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