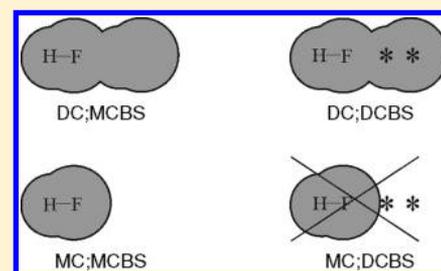


# On the Calculations of Interaction Energies and Induced Electric Properties within the Polarizable Continuum Model

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## S Supporting Information

**ABSTRACT:** In this work we investigate the influence of a polarizable environment on the interaction energies and the interaction-induced (excess) static electric dipole properties for the selected model hydrogen-bonded complexes. The excess properties were estimated for water and hydrogen fluoride dimers using the supermolecular approach and assuming the polarizable continuum model (PCM) as a representation of the polarizable environment. We analyze in this context the performance of the counterpoise correction and the consequences of various possible monomer cavity choices. The polarizable environment reduces the absolute magnitudes of interaction energies and interaction-induced dipole moments, whereas an increase is observed for the absolute magnitudes of induced polarizabilities and first hyperpolarizabilities. Our results indicate that the use of either monomeric (MC) or dimeric (DC) cavities in calculations of monomer properties does not change qualitatively the resultant excess properties. We conclude that the DC scheme is more consistent with the definition of the interaction energy and consequently also the interaction-induced property, whereas the MC scheme corresponds to the definition of stabilization energy. Our results indicate also a good performance of the counterpoise correction scheme for the self-consistent methods in the case of all studied properties.



## INTRODUCTION

Drafting materials with desirable optical properties begins at the molecular level. Nowadays, the available theoretical approaches of quantum chemistry allow us to calculate the molecular electric properties with relatively good accuracy,<sup>1–3</sup> and various methods have been proposed to estimate the electrooptical quantities of the bulk materials.<sup>4</sup> For instance, in the simplest approximation, which is the so-called “oriented gas” model, electric properties of the molecular crystal can be estimated as a sum of the respective properties of constituent molecules. Unfortunately it has been shown that quite often such an approach is not adequate for quantitative predictions.<sup>4</sup> This is due to pairwise and non-additive interactions which influence the optical response of a material.

Particularly interesting in this context are the hydrogen-bonded complexes whose properties differ significantly from the sum of the molecular properties.<sup>5–10</sup> However, it is difficult to compare computational results obtained for isolated gas-phase complexes directly with experimental data, particularly in the case of molecular hyperpolarizabilities. It is not only because various experimental techniques usually measure some rotational averages or vector components of some tensor properties but also because the experimental intensities are related to an effective molecular property by a series of complicated sample-dependent factors.<sup>11</sup> Moreover, the measurements are usually performed for bulk materials in which the molecules of interest always appear in a polarizable environment that influences their physical and chemical properties.<sup>12,13</sup>

It has been shown, for instance, that different solvents can significantly alter the measured hyperpolarizability of a molecule (in the case of *p*-nitroaniline even by a factor of 2).<sup>1</sup> Therefore it might be interesting to establish how and to what extent the polarizable environment influences the effects attributed to hydrogen bonding.

Although, the influence of polarizable environment on the intermolecular interaction energies<sup>14–24</sup> and, occasionally, also on their components<sup>25–28</sup> has been investigated in many theoretical studies, we are not aware of any ab initio studies of these effects in the case of interaction-induced electric properties.

There are many approximate models of solvent suitable for such investigations. In principle, one could divide them into discrete and continuous models.<sup>13,18,29</sup> Both approaches have their advantages and disadvantages. The discrete models explicitly account for the interactions of the solute with a limited number of solvent molecules. On the other hand they usually neglect the rotational averaging of these interactions which, in turn, are easily accounted for in the continuous models. This, however, comes at a price of a more approximate representation of solvent and, consequently, also the specific solute–solvent interactions like hydrogen bonds. Nevertheless, for this study we have chosen the polarizable continuum

Received: February 20, 2012

Revised: April 6, 2012

Published: April 6, 2012

model<sup>18</sup> (PCM) which belongs to the latter category. Our choice was dictated primarily by the fact that this model has been applied in most of the aforementioned studies of the intermolecular interactions in solution. Moreover, it has also been successfully applied in many studies of molecular (hyper)polarizabilities.<sup>2,30–37</sup>

In the previous study<sup>27</sup> some of us have investigated the influence of polarizable environment on the interaction energies and their components using various approximate models of solvent. In this work we wish to extend these studies and investigate in this context the interaction-induced static electric dipole properties for the same model hydrogen-bonded dimers of hydrogen fluoride and water. Moreover, we wish to test in this regard the performance of the counterpoise correction<sup>38</sup> and comment on the appropriateness of various possible choices of monomer cavity shapes (“monomeric” vs “dimeric”).

## METHODOLOGY

All the reported interaction energies and interaction-induced static electric properties were calculated using the Hartree–Fock method (HF), second-order Møller–Plesset perturbation theory (MP2), and the Kohn–Sham Density Functional Theory with M06-2X hybrid meta GGA functional in combination with the polarizable continuum model (PCM) as implemented in the Gaussian 09 package.<sup>39</sup> In the MP2 calculations with the PCM model the electron correlation energies were calculated for the HF reaction field (i.e., assuming the so-called PTE scheme<sup>40,41</sup>). The aug-cc-pVXZ (where X = D,T,Q) Dunning’s correlation-consistent basis sets were used in all calculations, which are hereafter abbreviated as AccX.<sup>42,43</sup>

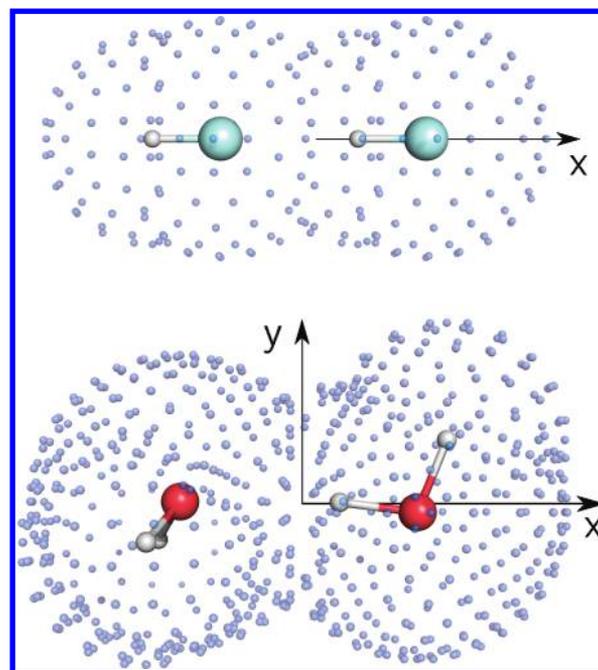
Contrary to our previous work,<sup>27</sup> in this study we analyze the linear HF dimer (oriented along *x*-axis) which structure has been taken from the paper published by Turi and Dannenberg.<sup>44</sup> Although this structure does not correspond to the global minimum it is more suitable for a model study of excess static electric properties. This is due to its axial symmetry which allows to attribute the interaction-induced changes of the vector component of first hyperpolarizability (being an experimentally measurable quantity, cf. Davidson et al.<sup>45</sup>) directly to hydrogen bonding. In the case of water dimer, however, we retained the CCSD(T)/AccT gas-phase equilibrium geometry reported by Halkier et al. which was assumed in all calculations.<sup>46</sup> The structure and orientation of both complexes is shown schematically in Figure 1 along with a discrete representation of the solute–solvent interface (see later).

**Electric Properties.** The static electronic electric dipole properties reported in this study were calculated using the finite field (FF) method.<sup>47–49</sup> These properties are defined in terms of the following Taylor series expansions of the energy or dipole moment in an external electric field (assuming the Einstein Summation Convention):

$$E(F) = E(0) - \mu_i F_i - \frac{1}{2} \alpha_{ij} F_i F_j - \frac{1}{6} \beta_{ijk} F_i F_j F_k + \dots \quad (1)$$

$$\mu_i(F) = \mu_i(0) + \alpha_{ij} F_j + \frac{1}{2} \beta_{ijk} F_j F_k + \dots \quad (2)$$

In the above equations,  $E(0)$  and  $\mu(0)$  are the energy and permanent dipole moment of a molecule in the absence of an electric field  $F$ , while  $\alpha_{ij}$  and  $\beta_{ijk}$  are the components of the



**Figure 1.** Geometries and orientation of the studied hydrogen-bonded dimers. Small blue dots represent the actual centers of spherical Gaussian functions of the solvent excluded surface in which the apparent surface charge was expanded in continuous surface charge PCM calculations.

polarizability, and first hyperpolarizability tensors, respectively. All tensor elements of the studied electric dipole properties were computed using the central-difference formulas as implemented in Gaussian 09.<sup>39</sup> On the basis of the results of Rutishauser–Romberg analysis<sup>50,51</sup> we have found that the region of stability falls for fields in the range 0.0008–0.0016 au, which is why the base field 0.001 au has been used in calculations of all the required field dependent energies.

The static interaction-induced electric dipole properties studied in this work can be defined as excess properties of a complex. For a dimer AD these can be calculated in the supermolecular approach as a difference of a given property of the complex and those of its constituents.

$$\Delta P_{AD} = P_{AD} - P_A - P_D \quad (3)$$

To elucidate the effects of hydrogen-bonding interactions we analyze the components of dipole moment parallel to the H-bond direction ( $\mu_x$ ), the corresponding vector components of the first hyperpolarizability ( $\beta_x$ ), and the average polarizabilities ( $\alpha_0$ ). The following formulas were used to determine the magnitudes of studied (hyper)polarizabilities for the all-static field case:

$$\alpha_0 = \frac{1}{3} \sum_{i=x,y,z} \alpha_{ii} \quad (4)$$

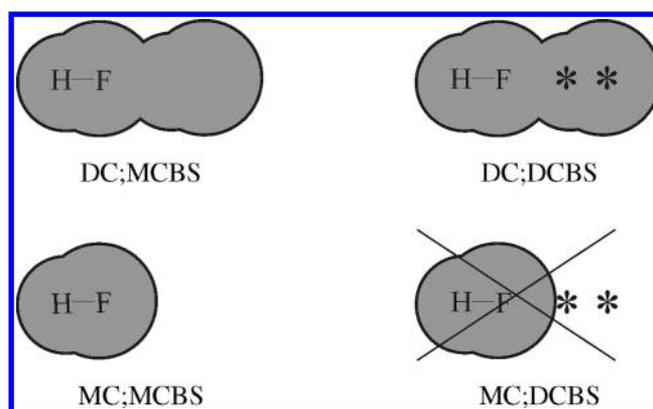
$$\beta_x = \frac{3}{5} \sum_{i=x,y,z} \beta_{xii} \quad (5)$$

In the case of linear hydrogen fluoride dimer  $-\beta_x$  is the projection of first hyperpolarizability tensor along the permanent dipole moment direction (often denoted as  $\beta_\mu$ ), whereas in the case of water dimer the two quantities should have very similar magnitude since the dipole moment vector

nearly coincides with the  $x$ -axis. For instance our best estimate of the water dimer's dipole moment vector in the gas phase, obtained using the MP2/AccQ method, is  $\vec{\mu} = (-1.024, 0.016, 0.000)$  au, and the magnitudes of  $\beta_x$  and  $\beta_\mu$  amount to 6.53 and  $-6.58$  au, respectively. The corresponding values of  $\beta_\mu$  obtained for both monomers amount to  $-17.0$  au and compare well with the gas-phase experimental (EFISH) estimate of  $-19.2 \pm 0.9$  au.<sup>11</sup> Our best estimates are also very close to the state-of-the-art results of Maroulis, who at the CCSD(T) level obtained  $-17.5$  and  $-6.3$  au for  $\beta_\mu$  of water molecule and dimer, respectively.<sup>5</sup>

**Interaction and Stabilization Energies of Complexes in the Polarizable Continuum Model.** To account for the influence of the polarizable environment on the studied properties the conductor-like formalism for the polarizable continuum model (C-PCM) was applied.<sup>18,52,53</sup> In this model solvent is treated as a structureless polarizable medium characterized primarily by its dielectric constant  $\epsilon$ . The solute, treated at the ab initio level, is placed within a cavity usually formed by a set of interlocking spheres centered on atoms or atomic groups.<sup>54</sup> In this work we use the recently proposed continuous surface charge (CSC) approach<sup>55</sup> in which the apparent surface charge is expanded in terms of spherical Gaussian functions located at the discretized solvent excluded surface approximated by the GePol algorithm (see Figure 1). Although Scalmani and Frisch suggested a surface defined from the UFF radii scaled by a factor of 1.1 as the most general,<sup>55</sup> we decided to use the previously recommended spheres of van der Waals radii scaled by a factor of 1.2 and centered on all atoms (including hydrogens).<sup>56,57</sup> In the calculations with the PCM model we included only the electrostatic contribution and assumed the dielectric constant of liquid water ( $\epsilon = 78.3553$ ); however, for the selected method (MP2/AccQ) we investigated also the dependence of the studied properties on  $\epsilon$ .

Since all calculations of the excess properties were performed using the supermolecular approach and finite basis sets, the results suffer from the basis set superposition error (BSSE). To estimate the BSSE-free properties the full counterpoise correction (FCP) scheme due to Boys and Bernardi<sup>39</sup> is commonly applied. However, in the case of PCM calculations one has to make an additional arbitrary choice as to the shape of cavities used in calculations of monomer properties. In the previous studies the dimeric cavities (DC) were usually assumed because of an apparent analogy to the counterpoise procedure.<sup>19,25,58</sup> However, in our recent study<sup>27</sup> we argued that only such a choice of cavity is, in fact, consistent with the definition of interaction energy (see Figure 2), which within the Born–Oppenheimer approximation is the difference between the energy of a complex and those of its constituents, each estimated at the geometry assumed in complex (cf. Szalewicz and Jeziorski<sup>59</sup>). Consequently, an alternative approach in which the energies of each of the monomers are computed in their respective monomeric cavities (MC) would be consistent with the definition of stabilization energy.<sup>59</sup> In this respect the differences between the two schemes could be identified as the energetic cost of structural reorganization of solvent during the dissociation of a complex in a solution (similarly to the structural relaxation of interacting species which can be defined as the difference of the stabilization and interaction energies). Naturally the above reasoning could also be generalized to other excess properties computed using the MC or DC schemes.



**Figure 2.** Schematic diagram of various schemes used for calculations of monomer properties under an influence of polarizable dielectric medium (PCM) shown on the example of HF dimer: dimeric cavities (DC) and monomeric cavities (MC) with monomer (MCBS) or dimer centered basis sets (DCBS). The use of DCBS basis set with monomer cavity is assumed to be invalid within the PCM model.

It should be noted that even though both interaction and stabilization energies are theoretically well-defined, they are not directly measurable, and in principle they should be supplemented at least by the zero-point vibrational correction to be related to the dissociation energy of the complex.<sup>59</sup> Actually, there is an ongoing discussion in the literature about how this should be done within continuum solvation models.<sup>60,61</sup> The recent results indicate, however, that in the case of hydrogen-bonded complexes the PCM model predicts a reliable solvation contribution to the complexation Gibbs free energies.<sup>24</sup>

In this study we compare and discuss the results of the interaction and stabilization (free) energies computed in vacuum (VC) and in the PCM model using DC and MC schemes, respectively:

$$\Delta G_{AB}^{\text{int}} = G_{AB}(\text{DC}) - G_A(\text{DC}) - G_B(\text{DC}) \quad (6)$$

$$\Delta G_{AB}^{\text{st}} = G_{AB}(\text{DC}) - G_A(\text{MC}) - G_B(\text{MC}) \quad (7)$$

The term *free energy* is used here to underscore the fact that the energies of all subsystems in the PCM model are obtained, conceptually, through a reversible charging process.

Since we are not aware of any previous systematic studies of the performance of the two schemes, particularly in the context of electric properties, we report also the excess static electric properties estimated using both schemes and analyze the performance of counterpoise correction procedure (FCP). It should be noted, however, that since some of the studied properties are tensors, it is more convenient to use in all calculations the same geometries of monomers—also in the MC scheme, even though the relaxed geometries would be more appropriate in this case. Although in doing so we neglect the effects of geometry relaxation of the monomers at an infinite separation, this effect is expected to be rather small for the studied systems.<sup>27</sup>

It should also be noted that in this work we do not report any quantities computed using monomeric cavities in combination with the dimer centered basis set (MC;DCBS). That is because such an approach would inevitably lead to a substantial charge density lying outside the cavity and hence a violation of the boundary conditions imposed on Poisson equation in the PCM model.<sup>62</sup>

**Table 1.** Selected Electric Properties of the Studied Complexes and of Their Constituents Calculated Using Various Theoretical Approaches and the AccQ Basis Set in Vacuum (VC) and under an Influence of Polarizable Environment Represented by the PCM Model with Different Variants of Monomer Cavities (MC and DC)<sup>a</sup>

	HF				MP2				M06-2X			
	$P_A$	$P_D$	$P_{AD}$	$\Delta P_{AD}$	$P_A$	$P_D$	$P_{AD}$	$\Delta P_{AD}$	$P_A$	$P_D$	$P_{AD}$	$\Delta P_{AD}^b$
Hydrogen Fluoride Dimer												
$\mu_x$												
VC/MCBS	-0.760	-0.760		-0.169	-0.713	-0.713		-0.176	-0.725	-0.725		-0.180
VC/DCBS	-0.759	-0.760	-1.689	-0.170	-0.713	-0.713	-1.602	-0.176	-0.725	-0.725	-1.630	-0.180
MC/MCBS	-0.862	-0.862		-0.119	-0.819	-0.819		-0.127	-0.831	-0.831		-0.133
DC/MCBS	-0.855	-0.849		-0.139	-0.813	-0.805		-0.147	-0.824	-0.817		-0.154
DC/DCBS	-0.854	-0.849	-1.843	-0.140	-0.813	-0.805	-1.765	-0.147	-0.824	-0.817	-1.795	-0.154
$\alpha_0$												
VC/MCBS	4.89	4.89		-0.02	5.59	5.59		0.00	5.49	5.49		0.05
VC/DCBS	4.89	4.89	9.76	-0.02	5.60	5.59	11.18	-0.01	5.50	5.49	11.03	0.04
MC/MCBS	5.47	5.47		0.02	6.33	6.33		0.06	6.22	6.22		0.11
DC/MCBS	5.43	5.46		0.07	6.29	6.31		0.12	6.18	6.20		0.17
DC/DCBS	5.44	5.46	10.96	0.06	6.30	6.32	12.72	0.10	6.19	6.20	12.55	0.16
$\beta_x$												
VC/MCBS	6.3	6.3		-3.8	8.1	8.1		-5.5	7.5	7.5		-4.7
VC/DCBS	5.8	6.3	8.8	-3.3	7.3	8.0	10.7	-4.6	6.8	7.4	10.3	-3.9
MC/MCBS	4.6	4.6		-4.4	6.0	6.0		-6.9	5.1	5.1		-6.1
DC/MCBS	4.6	4.8		-4.6	5.8	6.3		-7.0	5.1	5.5		-6.5
DC/DCBS	4.0	4.8	4.8	-4.0	4.7	6.2	5.1	-5.8	4.2	5.4	4.1	-5.5
Water Dimer												
$\mu_x$												
VC/MCBS	-0.448	-0.394		-0.219	-0.420	-0.370		-0.234	-0.428	-0.376		-0.237
VC/DCBS	-0.448	-0.394	-1.061	-0.219	-0.420	-0.370	-1.024	-0.234	-0.428	-0.376	-1.041	-0.237
MC/MCBS	-0.528	-0.465		-0.171	-0.505	-0.445		-0.187	-0.512	-0.451		-0.193
DC/MCBS	-0.510	-0.448		-0.206	-0.485	-0.426		-0.226	-0.493	-0.433		-0.230
DC/DCBS	-0.510	-0.448	-1.164	-0.206	-0.486	-0.427	-1.137	-0.224	-0.493	-0.433	-1.156	-0.230
$\alpha_0$												
VC/MCBS	8.50	8.50		-0.05	9.65	9.65		0.03	9.43	9.43		0.10
VC/DCBS	8.53	8.52	16.95	-0.10	9.71	9.68	19.33	-0.06	9.47	9.45	18.96	0.04
MC/MCBS	9.88	9.88		0.11	11.36	11.36		0.27	11.10	11.10		0.36
DC/MCBS	9.82	9.83		0.22	11.29	11.29		0.41	11.03	11.03		0.50
DC/DCBS	9.86	9.84	19.87	0.17	11.36	11.32	22.99	0.31	11.08	11.06	22.56	0.42
$\beta_x$												
VC/MCBS	6.4	5.6		-9.0	9.8	8.6		-11.9	8.5	7.5		-11.7
VC/DCBS	6.1	5.9	3.0	-9.0	9.2	9.2	6.5	-11.9	8.2	8.0	4.3	-11.9
MC/MCBS	2.9	2.5		-10.8	5.1	4.5		-16.5	4.1	3.7		-18.0
DC/MCBS	4.6	2.9		-12.9	7.3	5.2		-19.4	6.0	4.3		-20.5
DC/DCBS	3.9	3.0	-5.4	-12.3	5.8	5.5	-6.9	-18.2	5.0	4.4	-10.2	-19.6

<sup>a</sup>All electric properties are in atomic units. <sup>b</sup> $P_A$  is the property of proton acceptor A,  $P_D$  is the property of proton donor D,  $P_{AD}$  is the property of dimer AD, whereas  $\Delta P_{AD}$  is the corresponding excess property.

$$-\nabla^2 V(\vec{r}) = 4\pi\rho_M(\vec{r}) \quad \text{inside cavity} \quad (8)$$

$$-\epsilon\nabla^2 V(\vec{r}) = 0 \quad \text{outside cavity} \quad (9)$$

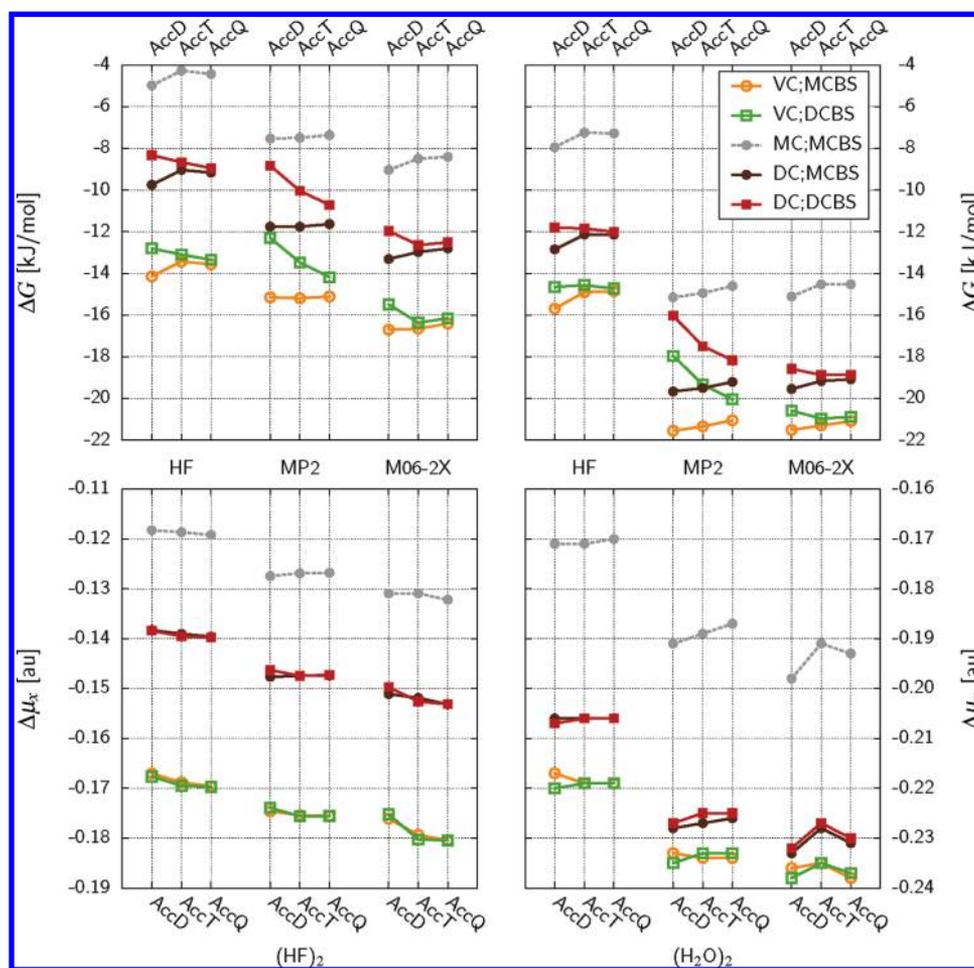
## RESULTS AND DISCUSSION

Our best estimates of the free energies of interaction and stabilization as well as the interaction-induced static electric properties and the corresponding total properties of complexes and their subsystems are given in Table 1. The basis set extension effects are plotted in Figures 3–4 while the underlying numerical values can be found in the Supporting Information to this paper.

In general, the differences in corresponding magnitudes obtained using MCBS and DCBS schemes allow to estimate the basis set superposition error (BSSE). Since in all

calculations performed for isolated monomers their geometrical parameters were kept fixed at those assumed in the complex, a comparison of the results obtained using MC;MCBS and DC;MCBS schemes will allow, regardless of the context, to estimate the impact of cavity construction on the analyzed properties.

**Interaction vs Stabilization Energies in Polarizable Environment.** In the case of both studied dimers the presence of polarizable environment leads to a considerable weakening of their free energies of interaction  $\Delta G^{\text{int}}$ . In the case of hydrogen fluoride dimer the  $\Delta G^{\text{int}}$  estimated at the HF level is reduced by about 30% whereas in the case of water dimer by about 20% with respect to the corresponding gas-phase interaction energies (Figure 3). The electron correlation diminishes this effect by about 10% consistently for both tested methods (MP2 and M06-2X). However, our best



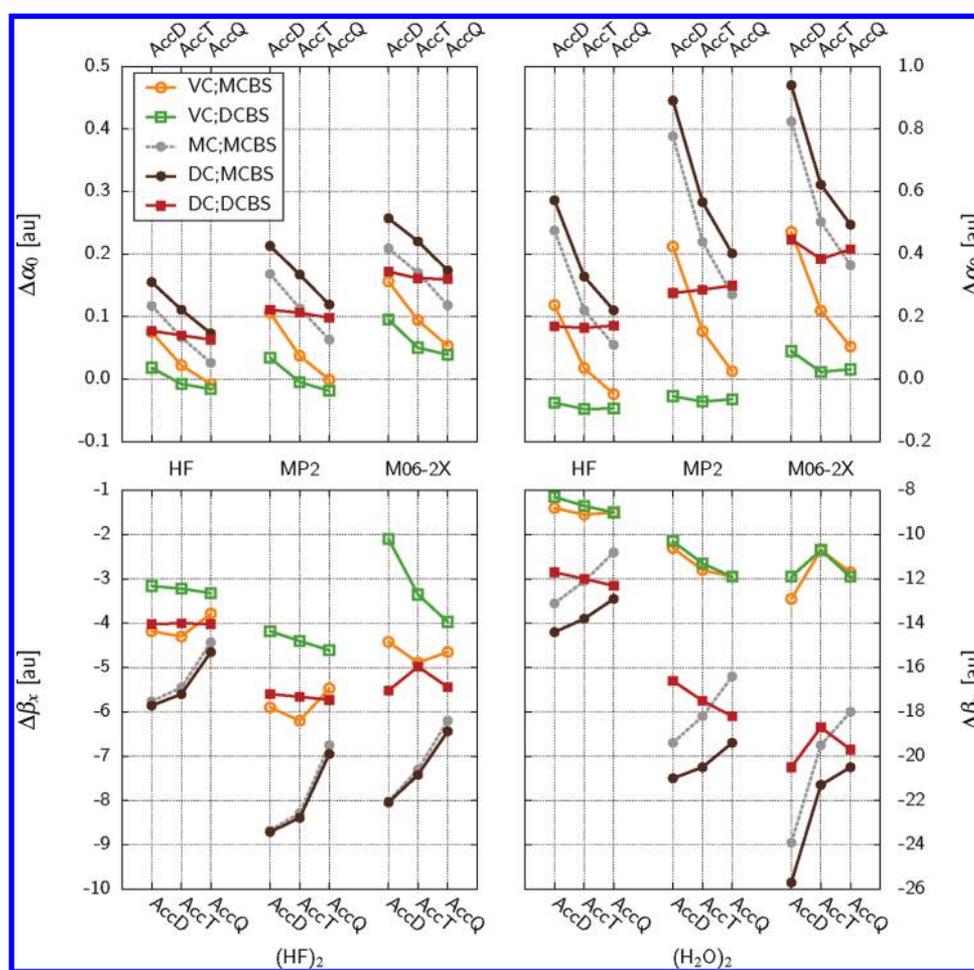
**Figure 3.** Interaction and stabilization (free) energies and the corresponding interaction-induced dipole moments ( $\Delta\mu_x$ ) of hydrogen fluoride (left column) and water (right column) dimers in gas-phase (VC) and polarizable environment estimated using various theoretical methods. Acronyms DC and MC stand for dimeric and monomeric cavities, respectively, whereas MCBS and DCBS denote monomer and dimer centered basis sets. In the case of energies the MC results correspond to  $\Delta G^{\text{st}}$  whereas the DC results denote the BSSE corrected (DCBS) or uncorrected (MCBS)  $\Delta G^{\text{int}}$  (cf. equation 6).

estimates of the stabilization energies  $\Delta G^{\text{st}}$  indicate that the influence of a highly polarizable environment could reduce the strength of the hydrogen bond to only half of its gas-phase strength. These results are consistent with those obtained recently by Lipparini et al. for base pair dimers, where the reduction was even more substantial,<sup>23</sup> and positive dimerization free energies of carboxylic acids in water reported by Colominas et al.<sup>14</sup>

All the above conclusions remain valid regardless of whether we use the counterpoise correction or not. However, in the case of MP2 results the counterpoise correction seems to worsen instead of improve the results with respect to the basis set limit, particularly for the smallest basis set. This effect is not related to the use of an approximate model of solvent as it is observed also in vacuum (VC). It is a well-known phenomenon described already in the literature.<sup>63,64</sup> Nevertheless, the electron correlation influences significantly the discussed quantities (particularly in the case of water dimer). It should be underscored, however, that the relative differences between  $\Delta E^{\text{int}}$  in vacuum and  $\Delta G^{\text{int}}$  or  $\Delta G^{\text{st}}$  in dielectric medium remain virtually unaffected by the level of theoretical approximation. Especially the differences between  $\Delta G^{\text{st}}$  and  $\Delta G^{\text{int}}$  remain almost constant for both studied systems and for all methods used, with the magnitude of stabilization energy smaller by

about 4 kJ/mol than the corresponding interaction energy. An interesting observation is the fact that the magnitudes of the counterpoise correction estimated in vacuum and polarizable environment for a given basis set are nearly the same. This confirms the validity of the assumptions made by Lipparini et al. who corrected the interaction energies estimated in aqueous solution (using PCM model) for counterpoise correction estimated in the gas-phase.<sup>23</sup> An excellent performance of M06-2X method should also be noted with regards to the counterpoise correction (there is no overcorrection observed for MP2 method) and semiquantitative quality of the results obtained already in the smallest basis set.

**Dipole Moments.** The intermolecular interactions have opposite effects on the dipole moments of both studied complexes since they increase the polarity of the water dimer while a decrease is observed for the hydrogen fluoride dimer (see Figure 3 and Table 1). This conclusion remains valid both in the gas-phase and in the polarizable environment, even though the mutual interactions with the latter result in more polar complexes. Also the absolute magnitudes of  $\Delta\mu_x$  are generally diminished; however, a much larger extent of this effect is observed when monomeric cavities are used in calculations of monomer properties instead of dimeric ones. This is an expected result since the interactions of monomers



**Figure 4.** Excess average polarizabilities ( $\Delta\alpha_0$ ) and first hyperpolarizabilities ( $\Delta\beta_x$ ) of hydrogen fluoride (left column) and water (right column) dimers calculated in gas-phase (VC) and polarizable environment using various theoretical methods. Acronyms DC and MC stand for dimeric and monomeric cavities used in monomer calculations, respectively, whereas MCBS and DCBS denote monomer and dimer centered basis sets.

with the dielectric environment are much stronger in this case. Interestingly, the relative differences of  $\Delta\mu_x$  determined using MC and DC schemes virtually do not depend on the choice of theoretical method, similarly as in the case of the excess free energies discussed above.

The electron correlation effects are qualitatively and quantitatively similar in the case of MP2 and M06-2X results, and generally they lead to an increase of the absolute magnitudes of the excess dipole moments. Moreover, the basis set superposition error seems to be a parameter of marginal importance in this case, having virtually no effect on the magnitudes of the studied excess properties. This observation is consistent with our previous reports regarding interaction-induced dipole moments of complexes in the gas phase.<sup>65</sup>

**Polarizability.** The molecular polarizabilities are nearly additive for the studied systems (particularly for HF dimer) and the estimated relative influence of intermolecular interactions remains in most cases well below 2% (Table 1). Hence, it is difficult to draw any more general conclusions based on these data. Nevertheless, the presence of dielectric environment induces a substantial relative increase of polarizabilities of interacting species as well as the interaction-induced contributions. The excess properties estimated within the PCM model using the MC and DC schemes (Figure 4) are very close to each other, with the DC results slightly above MC (contrary

to the effects observed for the corresponding values of  $\Delta G$  and  $\Delta\mu_x$ ). This reversed ordering of results obtained using MC and DC schemes is quite surprising since one would expect that the use of larger dimeric cavities in calculations of molecular properties should result in greater polarizabilities than in the case of monomeric cavities and, hence, relatively smaller  $\Delta\alpha_0$ . Nevertheless, we observe such an effect consistently for both studied complexes and all tested methods. One should note also an excellent performance of the counterpoise correction in producing quantitatively correct results (both in the gas phase and in solvent) even in the case of MP2 results (see Figure 4).

**First Hyperpolarizability.** Since water dimer at its gas-phase equilibrium geometry does not have an axial symmetry we decided in the case of both studied systems to analyze the influence of intermolecular interactions and polarizable environment on the projection of the first hyperpolarizabilities on the direction of hydrogen bond ( $\beta_x$ ). The results are reported in Figure 4 and Table 1.

The intermolecular interactions reduce substantially the gas-phase hyperpolarizability of hydrogen fluoride dimer with respect to the sum of isolated monomer properties. This effect is increased when passing to the solvent by as much as 37% (M06-2X/AccQ results). Moreover, the polarizable environment leads also to a substantial decrease of the properties of interacting species and in effect the  $\beta_x$  of a complex could be reduced even to 40% of its gas-phase magnitude according to

M06-2X/AccQ results. The MP2 and DFT results are consistent in this respect; however, the overall influence of electron correlation effects is rather small for this system and qualitatively similar results are obtained also at the HF level. For this complex there is also virtually no difference between the PCM results obtained using MC and DC schemes at all levels of theoretical approximation. Again, the performance of counterpoise correction is very good with a possible exception of the gas-phase M06-2X results for which it leads to a deteriorating quality of the results obtained for small basis sets.

In the case of water dimer we observe qualitatively similar effects of intermolecular interactions as for hydrogen fluoride; however, the reduction of the complex' first hyperpolarizability is even more substantial ( $\Delta\beta_x$  is much larger than  $\beta_x$  of the dimer itself). The influence of polarizable environment is also similar and leads to a further increase of absolute magnitude of  $\Delta\beta_x$  by as much as 60% for M06-2X/AccQ results. As a result the overall property of the complex changes qualitatively from slightly positive to significantly negative value. A similar effect is observed for all tested methods; however, its extent is greater in the case of M06-2X/AccQ results, for which  $\beta_x$  of the complex changes from 4.3 au in the gas phase to  $-10.2$  au when passing to the solvent. Since the corresponding  $\Delta\beta_x$  amounts to  $-19.6$  au, the influence of intermolecular interactions on the studied property is huge (more than 90%). Interestingly, in the case of gas-phase results obtained for water dimer using all tested methods the counterpoise correction is relatively small and, it becomes much larger in the polarizable environment. Still the performance of counterpoise correction is rather satisfactory, particularly for the self-consistent methods (HF and M06-2X), whereas for the MP2 method the relative errors are nearly the same whether we apply the correction or not, and the results are either overestimated or underestimated with respect to the apparent basis set limit. As far as the choice of monomer cavity in the PCM calculations is concerned, qualitatively similar results are obtained using both MC and DC schemes, with the latter being always slightly larger than the former (similarly as in the case of excess polarizabilities).

## CONCLUSIONS

We have analyzed the influence of polarizable environment represented by the PCM model on the interaction energies and the interaction-induced electric properties of two model hydrogen-bonded complexes. In general, the polarizable environment reduces the absolute magnitudes of interaction free energies and interaction-induced dipole moments with respect to the gas-phase estimates, whereas an increase is observed for the absolute magnitudes of induced polarizabilities and first hyperpolarizabilities (often substantial cf.  $\Delta\beta_x$  of water dimer).

Although the use of monomeric (MC) or dimeric (DC) cavities in calculations of monomer properties changes the results quantitatively, the observed effects of polarizable environment are generally qualitatively consistent. In fact, we argue that the DC scheme is more consistent with the definition of the interaction energy and consequently interaction-induced property, whereas the MC scheme corresponds to the definition of stabilization energy. Nearly constant differences of the corresponding properties estimated using both schemes, regardless of the ab initio or DFT method used for calculations, also speak in favor of this assertion. Therefore the choice of a particular scheme should depend on the context. We only recommend against using of monomeric

cavities in combination with the dimer centered basis set (MC;DCBS), since this would lead to a violation of the boundary conditions imposed on Poisson equation in the PCM model.

Our results also indicate a good performance of the counterpoise correction scheme for the self-consistent methods (HF and DFT) in the case of all studied properties. However, in the case of some MP2 results it can lead to deterioration of the results obtained in unsaturated basis sets (e.g.,  $\Delta E^{\text{MP2}}$  and  $\Delta G^{\text{MP2}}$ ). Nevertheless, this deterioration is only quantitative, and the qualitative interpretation of the results does not change. An interesting observation is also the fact that the magnitudes of counterpoise correction estimated in vacuum and polarizable environment for a given basis set are nearly the same.

Although in the above discussion we focused on the results obtained either in vacuum ( $\epsilon = 1$ ) or in the highly polarizable environment ( $\epsilon \approx 80$ ), we investigated the dependence of the studied properties on  $\epsilon$  using the MP2/AccQ method. The results plotted in the Supporting Information indicate that our conclusions are general, and even though the extent of the observed effects is gradually diminishing for less polarizable environments, qualitatively consistent effects are observed for  $\epsilon$  in an intermediate range.

## ASSOCIATED CONTENT

### Supporting Information

The numerical data plotted in Figures 3–4 and the PCM results obtained for different values of dielectric constant are available as Supporting Information to this paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The work was financed by a statutory activity subsidy from the Polish Ministry of Science and Higher Education for the Faculty of Chemistry of Wrocław University of Technology and a computational grant from the Wrocław Center for Networking and Supercomputing (WCSS). The allotment of computing time is hereby gratefully acknowledged.

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