Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supporting Information

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(Dated: August 30, 2016)

I. SUPPORTING INFORMATION

Besides the additional information and results shown in this document, input and output files of all calculations as well as the LibreOffice tables with the collected data used to generate the plots are available for download.

A. Excited-State Densities

Correlated ground- and excited-state densities are required to compute the respective reaction fields. Formally, these densities can be obtained from the respective wavefunctions, which corresponds to unrelaxed densities, or by computing the energy-derivative with respect to an electric field, yielding relaxed densities.[1] Within our implementation of ADC, excited-state densities are obtained via the intermediate-state representation (ISR) formalism consistent to the given order in perturbation theory.[2] ADC is not a linear response method, and these densities are not "relaxed" in the aforementioned sense (i.e. they do not include an explicitly calculated orbital relaxation). They nevertheless contain significant density relaxation effects, as demonstrated recently at second order,[3,4] provide an accurate description of vertical excitation energies in solution,[5] and are inexpensive to compute. To compute the densities, the converged ADC excited-state vectors are combined with the intermediate-state basis of the appropriate order, yielding an excited-state wave function. Eventually, the excited-state densities used for the PCM calculations are consistent to first order for ADC(1) and to second order for ADC(2). For the third order methods an efficient implementation of the ISR of corresponding order is not yet available. Therefore, the ISR of second order is used in combination with the third-order state vectors, which is the definition of the mixed ADC(3/2) approach, referred to as ADC(3) in the following. Accordingly, for all approaches involving a MP(3) ground state, the solute-solvent interaction is accounted for using MP(2) densities.

B. Approach for Broken-Symmetry Calculations

To converge the SCF calculations onto the desired broken-s a number of issues have to be addressed. Firstly, in calculations with low dielectric constants (1.01 and 2) or without a PCM, the symmetrically charged solution is energetically close (in the ethene cation only about 0.2 eV higher) and hence, the SCF algorithm occasionally fails to break the symmetry of the initial guess. To assure convergence of the SCF onto the desired state, we carry out a preliminary SCF calculation for a slightly distorted geometry in combination with a PCM and $\epsilon = 100$ (see input files). While the distortion ensures symmetry breaking, the high dielectric additionally stabilized the asymmetrically charged solution. The latter is employed as initial guess in the subsequent calculation for the symmetric geometry and the desired ϵ. To prevent a fall-back onto the symmetric solution, we additionally use the maximum-overlap method (MOM) starting in the first iteration step.[6] Another situation in which the MOM is absolutely necessary is the SCF calculation during the solvent-field iterations. Since this SCF calculation is carried out in the solvent-field of the charge-inverse FICT state, it tends to converge onto the charge-inverse solution with respect to the prior step, which is obviously much lower in energy. Here, the MOM helps to force the SCF to converge on the energetically higher lying solution.

A different problem concerns the ADC calculation in highly polarizable environments. Due to the strong stabilization of the ground state in combination with the large separation of the monomers, the charge-inverse excited state is very high in energy regarding the Koopmans guess that is used by our ADC program to obtain an initial set of state vectors. Hence, despite the charge-inverse excited state always turning out as one of the lowest three or four excited states, one has to employ an unusually large number of guess vectors (40-80) for the ADC calculation, which in turn requires an even larger or at least as large subspace for the Davidson iterations. For the ethene and nitromethane dimers (232 and 324 basis functions, respectively) this does in combination with the requirement for an unrestricted calculation lead to prohibitively large memory requirements of several hundred gigabyte. Hence, we had to limit the level of theory for the solvent-field iterations for to the ADC(2)/cc-pVTZ level of theory for ethene, and to ADC(2)/cc-pVDZ for nitromethane.

C. Influence of the PCM Kernel

To investigate the influence of the PCM kernel we repeated the calculations at the MP2/PTED and

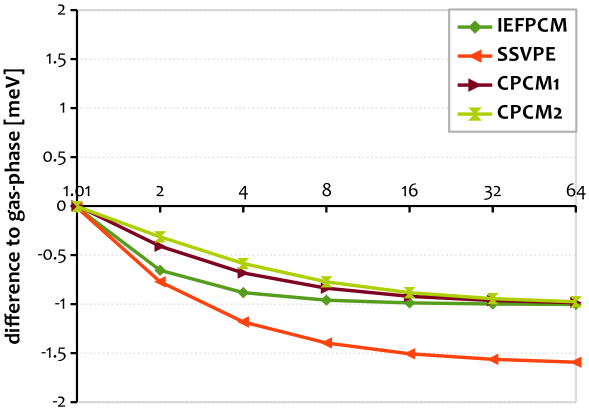

FIG. 1. Differences between the solvent-relaxed total energies of the ground state of the cationic ethene dimer computed with MP2/PTED and the charge-inverse excited state, computed with ADC(2)/EqS with the different PCM kernels as a function of ϵ (x-axis, logarithmic). The gas-phase difference of -0.34 eV (MP2−ADC(2)) has been subtracted. Mind the 5 times enlarged scale compared to the previous plot.

ADC(2)/EqS levels of theory for the ethene dimer radical cation with CPCM1, CPCM2 and SSVPE. The results for are shown in figure 1. In general, the differences between the PCM variants are very small and lie within 0.5 meV. However, while the curves obtained with CPCM1 and CPCM2 are virtually identical and, as expected, converge against each other and IEF-PCM in the strong dielectric regime, SSVPE yields a slightly but systematically shifted result over the whole range. Although the difference merely amounts to 0.5 meV for $\epsilon = 64$, it is surprising that SSVPE does not agree with with CPCM and IEF-PCM in the strong dielectric regime where all methods are supposed to be exact. This could be regarded as a one of a number of hint towards inconsistencies that have been reported for the SSVPE scheme in earlier work comparing the Pekar and Marcus partitions in the framework of PCM non-equilibrium corrections.[7]

D. Convergence of the Solvent-Field Iterations

To illustrate the convergence of the solvent-field equilibration procedure, we plotted the energy and energy change of ground and respective excited states for each step in figure 2) for the FICT states of the anionic ethene and nitromethane dimers with $\epsilon = 32$. Additionally, we computed and plotted the respective quantities for the prototypical charge-transfer state of N,N-dimethyl-4-nitroaniline (DMNA) with $\epsilon = 36.7$ as practical example. The energies of step 0 in fig. 2 A correspond to the MP2(PTE) ground-state and zeroth order (no ptSS) ADC(2) excited-state energies, which is used as the starting point of the solvent-field iterations.

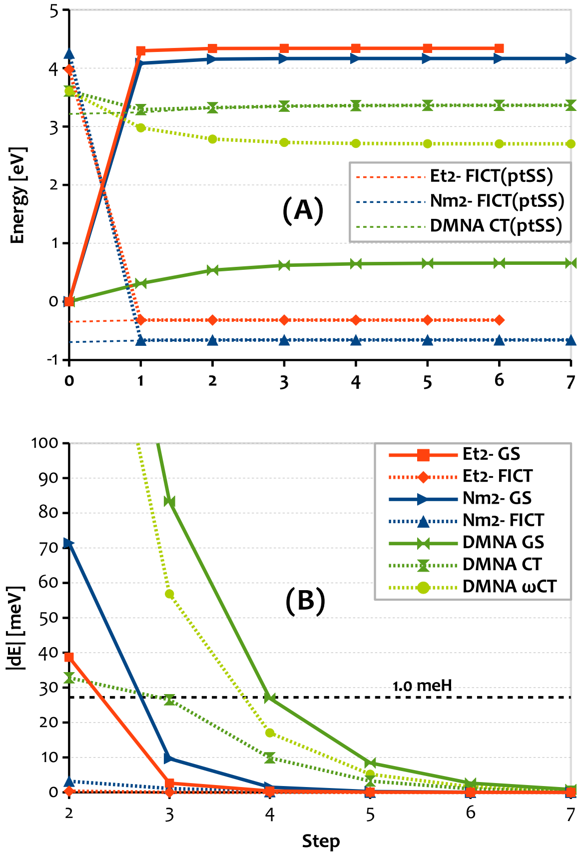

FIG. 2. **(A)**: Absolute energies, excitation energies (ω, DMNA only) and **(B)**: energy changes during the solvent-field iterations at the ADC(2)(EqS)/MP2 level of theory for the FICT states of the anionic ethene (cc-pVTZ) and nitromethane (cc-pVDZ) dimers as well as the CT state of DMNA (cc-pVDZ). The upper plot depicts the absolute energies with respect to the MP2(PTE) ground state and additionally the ptSS-corrected energies obtained with $\epsilon_{\text{opt}} = \epsilon$. The lower plot shows the energy-change with respect to the previous step starting at the second step. The geometry of DMNA was optimized at the SCS-MP2/cc-pVTZ level of theory with the COSMO solvation model and $\epsilon = 36.7$.

Despite the huge jump of 4–5 eV in the first step of the solvent-field iterations for the dimers, the respective ground and excited-state energies converge to change well below 1 meH within three steps. Within four (ethene) to five (nitromethane) steps, the energy change is below 1 meV. For DMNA the convergence is significantly slower than for the dimers. It takes 4-5 iterations until the energy-changes are well below 1 meH, and 7 iterations to converge to 1 meV. This is supposedly a result of the larger polarizability and more flexible electronic structure of this system.

Surprisingly, there is a large difference between the convergence of ground (solid lines) and excited-state (dotted lines) energies, whereas the excited-state energy converges much faster than the energy of the respective ground state. To further investigate this issue, we plotted also the zeroth order vertical excitation energy of DMNA in figure 2. Since ADC Hamiltonian is shifted by the ground-state energy, the method yields excitation energies, while for total excited-state energies the energy of the respective MP ground state is added. Keeping this in mind and regarding the run of the excitation-, excited- and ground-state energies for DMNA, it seems that changes in the ground-state and excitation energy largely cancel out, which eventually leads to a much faster convergence of the excited-state energy. While we can only speculate about the underlying reason, this observation has important implications for the practical application of the approach: To test if an ADC/EqS calculation is converged, one should check ground state and excitation energy, rather than the excited state energy. Hence, we convergence of our solvent-field iterations depends on SCF energies and differences in the charge-vector.

Besides these energies, also the ptSS corrections can be employed as a convergence criteria. Per definition, they constitute an estimate how the impact of a solvent-field relaxation impacts the energy and must hence vanish for any state in a fully relaxed solvent-field. Interestingly, this is the case only with the CPCM and IEFPCM kernels, but not with SSVPE, hinting towards an inconsistency of this approach. Similar findings have been reported in refs. 8 and[7].

In the calculations presented in this work we have used a fixed number of at least 5 solvent field iterations (after the symmetry-breaking and initial calculation of the RF) for the FICT state of the dimers, and at least 6 after the initial calculation of the RF for DMABN at the ADC(2) level of theory. To obtain the solvent-relaxed energies at the ADC(3) level of theory, we used 4 iterations at the ADC(2) level of theory followed by 5 iterations at the ADC(3) level of theory. The convergence of these calculations was monitored using the self-ptSS term of the respective, equilibrated state, which in all cases is well below 10^{-5} eV.

E. Solute-Solvent Interaction Energy in the Framework of the PTE, PTE-PTD and PTED approaches

To explore how the perturbatively correlation-corrected ground-state energy obtained with the PTE-PTD approach compares to the uncorrelated, self-consistent PTE and correlated, self-consistent PTED schemes, we compare the solute-solvent interaction energy of each of the approaches. While this quantity is well-defined for the PTE and PTE-PTD schemes, in which it is the interaction energy of the SCF or respectively MP density with the respective, self-induced polarization, its definition is not clear within the PTED and ADC/EqS schemes. In the latter, the SCF is computed in the field of a frozen reaction field computed for an MP or ADC density and the resulting MOs are used in an MP/ADC calculation (see fig. 1 in the manuscript). Hence, although the interaction with the correlated solvent field is introduced to the MOs at the SCF step, its influence onto the correlated density is implicitly accounted for during the subsequent MP/ADC calculation. Therefore, the energy of solvation of the EqS and PTED approaches does neither correspond directly to the interaction of the HF density with the correlated solvent field, nor to the self interaction of the MP/ADC density. We think, however, that the latter is more consistent with the definition for the PTE and PTE-PTD approaches and hence employ this definition.

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